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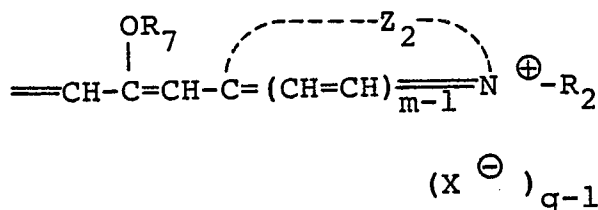
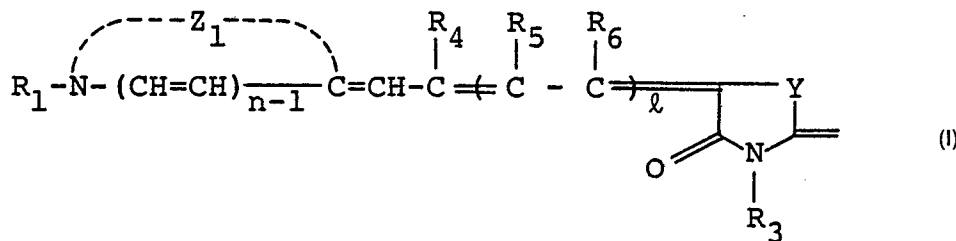
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⑤④ **Light sensitive materials for lithographic printing plates.**

57) Disclosed is a light sensitive material for lithographic printing plate which comprises a support and at least a silver halide emulsion layer and a surface physical development nuclei layer provided on said support wherein said

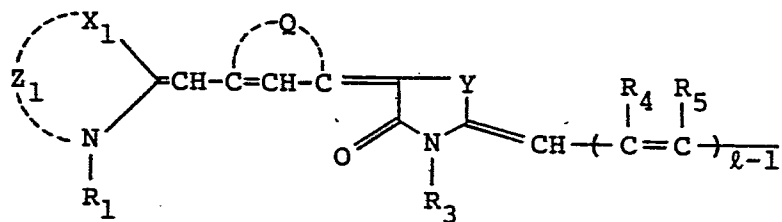
silver halide emulsion layer contains at least one of the sensitizing dyes represented by the following general formulas (I), (II), (III), (IV) and (V):

General formula (I)

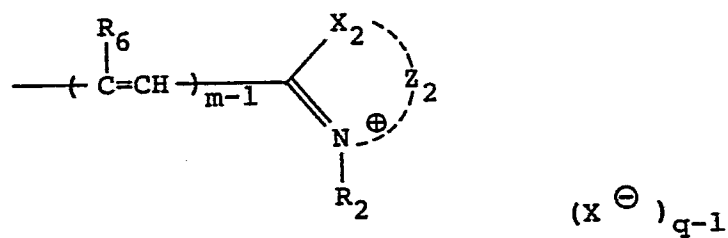


General formula (II)

0 230 100

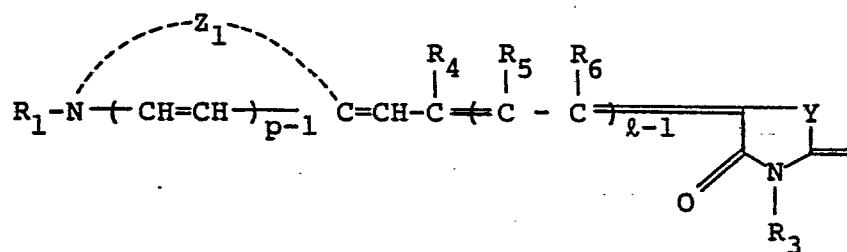


(II)

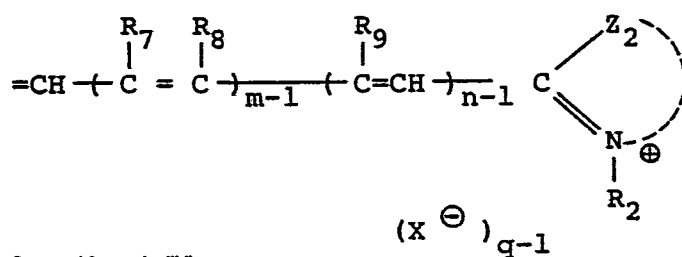


$(X^{\ominus})_{q-1}$

General formula (III)

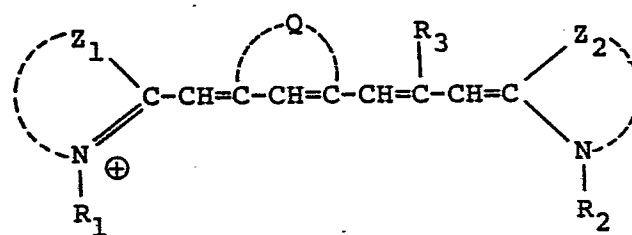


(III)



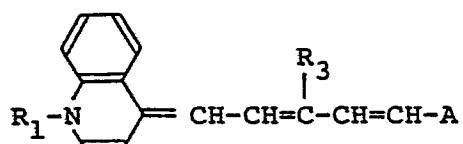
$(X^{\ominus})_{q-1}$

General formula (IV)



(IV)

$(X^{\ominus})_{q-1}$



(V)

$(X^{\ominus})_{q-1}$

LIGHT SENSITIVE MATERIALS FOR
LITHOGRAPHIC PRINTING PLATES

1 This invention relates to a silver halide photo-
graphic light sensitive material and more particularly it
relates to a silver halide photographic light sensitive
material which is spectrally sensitized for near-infrared
5 region by specific dyes.

 This invention is especially directed to a
lithographic printing plate which utilizes the silver
complex diffusion transfer process suitable for using semi-
conductor laser (or laser diode) beam as a light source and
10 a plate making method and a printing method using said
lithographic printing plate.

 Lithographic printing plates which use transfer-
red silver images formed by the silver complex diffusion
transfer process as ink receptive areas are disclosed in
15 Japanese Patent Examined Publication (Kokoku) No. 30562/73
and Japanese Patent Unexamined Publication (Kokai) Nos.
21602/78, 103104/79, 9750/81, etc. and they are well
known.

 According to a typical silver complex diffusion
20 transfer process suitable for making these lithographic
printing plates, a light sensitive material which comprises
a support and a subbing layer which serves also as an
anti-halation layer, a silver halide emulsion layer and a
physical development nuclei layer provided on said support
25 is exposed imagewise and developed, whereby silver halide

1 of latent image area becomes black silver in the emulsion
layer and simultaneously silver halide of non-latent image
area is dissolved by the action of a silver halide com-
plexing agent contained in a processing solution and
5 diffuses to the surface of the light sensitive material.
Thus dissolved and diffusing silver complex salt is
deposited as silver image on the physical development nuclei
in the surface layer by reducing action of developing
agent. Following the development, if necessary, the material
10 is subjected to a sensitizing treatment to increase ink
receptivity of the silver image. Then, thus obtained
lithographic printing plate was mounted on an offset
printing machine and printing is carried out by transferring
the inked image to a substrate.

15 According to the conventional method, the silver
halide emulsion layer is subjected to spectral sensitiza-
tion by a merocyanine or cyanine dye so that the emulsion
can have a sensitivity maximum in green radiation region
of near 550 nm and the emulsion is subjected to exposure
20 for several-several ten seconds by a process camera using
an ordinary light source such as tungsten light source.
Such conventional method, however, has a limit even when
the above-stated lithographic printing plates which are
inherently excellent in sharpness and resolution are used.
25 Besides, there are the problems that when a color print is
produced from a color original, not only the resolution is
still insufficient, but production of the light sensitive
material and making of lithographic printing plates are

1 complicated.

Use of laser beam for plate making has been proposed as a method for solution of the above problems. For example, lithographic printing plates to which helium-
5 neon laser or light emitting diode is applied are disclosed in U.S. Patent No. 4,501,811 and Japanese Patent Unexamined Publication (Kokai) Nos. 71055/84, 75838/85, 100148/85, etc. As also described in these patent documents, in the case of these lithographic printing plates which utilize
10 the silver complex diffusion transfer process, since the surface physical development nuclei layer gives a great effect on the spectral sensitization, the objective sensitivity to laser beam is reduced or shelf stability is deteriorated and moreover, since a low contrast transfer
15 silver image is precipitated by silver complex diffusion transfer development, sharpness and resolution are decreased and furthermore, there occur scumming of non-image area and dropout of silver image during printing, which make it impossible to obtain sufficient printing endurance. Thus,
20 it is difficult to make the desired lithographic printing plates of good quality. Therefore, a desired sensitizing dye should meet all of the following requirements:
sufficiently high sensitivity to the radiation wavelength from lasers; good shelf stability; formation of a high
25 contrast silver image; no adverse effect such as scumming; and formation of a transferred and precipitated silver having a sufficient strength to keep even small silver particles from dropping out during printing.

1 As for the lasers, there are known various types,
the method which uses laser sources such as helium-neon,
argon, etc. as those for scanner type have the defects
such as large and expensive devices required, low consump-
5 tion power efficiency, etc. On the other hand, semi-
conductor lasers have the advantages that they are small
in size and inexpensive, modulation can be easily performed
and they have a long shelf life. For the semiconductor
lasers, there are used such series of semiconductors as
10 Ga/As/P, Ga/Al/As, Ga/As, In/P, In/As, etc. and wavelength
of these laser beams is generally longer than 700 mμ and
mostly longer than 750 mμ.

Light sensitive materials for lithographic
printing plates which employ such semiconductor laser
15 beams of longer wavelength as light sources for image
exposure are disclosed in Japanese Patent Unexamined Publi-
cation (Kokai) No. 61752/85. This specification mentions,
as an especially preferred embodiment, a light sensitive
material for lithographic printing plate which comprises
20 a support and a non-silver light sensitive layer capable
of forming an oleophilic image (for example, comprising
an o-naphthoquinone compound) and a light sensitive
silver halide emulsion layer provided in this order on said
support and discloses sensitizing dyes represented by the
25 general formulas (I) - (IV) used in the above emulsion
layer and having a maximum spectral sensitivity in the
region longer than 700 mμ.

The inventors have made research on a lot of

1 infrared rays sensitizing dyes including those specifically
mentioned in the above patent specifications by adding
them to the silver halide emulsion layer of the above-
stated lithographic printing plates having a physical
5 development nuclei layer as an outermost surface layer.
As a result, they have found a group of sensitizing dyes
which can provide a sensitivity enough to perform plate-
making with semiconductor laser beam, a high resolving
power and a high printing endurance.

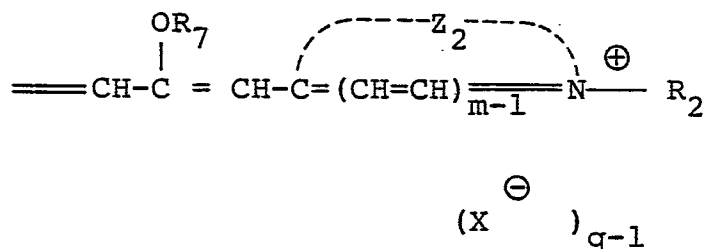
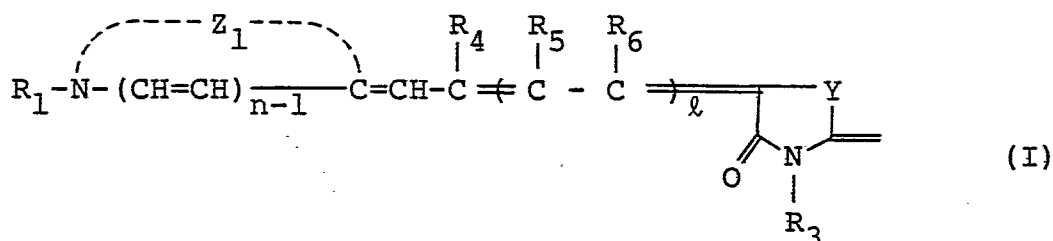
10 Accordingly, one object of this invention is to
provide a lithographic printing plate having a high
sensitivity which permit the use of a semiconductor laser
beam of low output, a high resolving power and a high
printing endurance and free from scumming, which utilizes
15 the silver complex diffusion transfer process, a plate
making method and a printing method.

Another object of this invention is to provide a
spectrally sensitized silver halide photographic light
sensitive material high in sensitivity to radiation of near-
20 infrared region, less in fog and furthermore, less in
reduction of sensitivity and formation of fog.

The above objects of this invention have been
achieved by containing the sensitizing dyes described here-
inbelow in a silver halide emulsion layer. That is, this
25 invention relates to a light sensitive material for
lithographic printing plates which comprises a support
and at least a silver halide emulsion layer and a surface
physical development nuclei layer provided on said support,

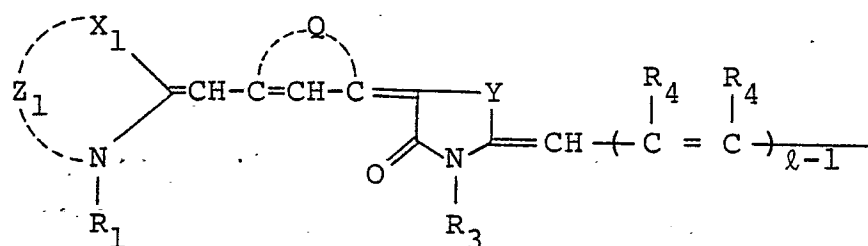
1 wherein said emulsion layer contains at least one of the sensitizing dyes represented by the following general formulas (I) - (V).

General formula (I):

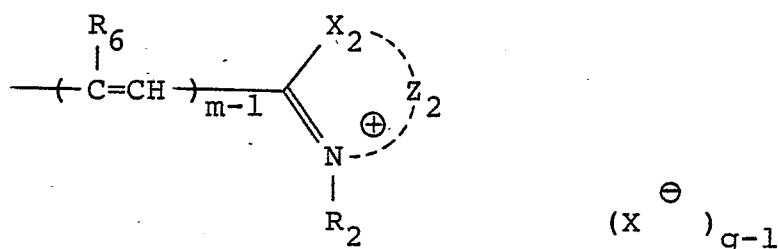


wherein Z_1 and Z_2 which may be identical or different
 5 represent a group of atoms which are necessary to form a 5- or 6-membered nitrogen containing heterocyclic ring;
 R_1 , R_2 and R_7 which may be identical or different represent alkyl group or alkenyl group; R_3 represents alkyl group, alkenyl group or aryl group; $R_4 - R_6$ which may be identical
 10 or different represent hydrogen atom, alkyl group or aryl group; ℓ represents 0 or 1 with a proviso that when ℓ is 1, R_4 and R_6 may link with each other to form a 5- or 6-membered ring; Y represents sulfur atom, oxygen atom or $>\text{N}-R_8$ (R_8 represents alkyl group); X represents acid anion;
 15 and m, n and q represent 1 or 2.

General formula (II):



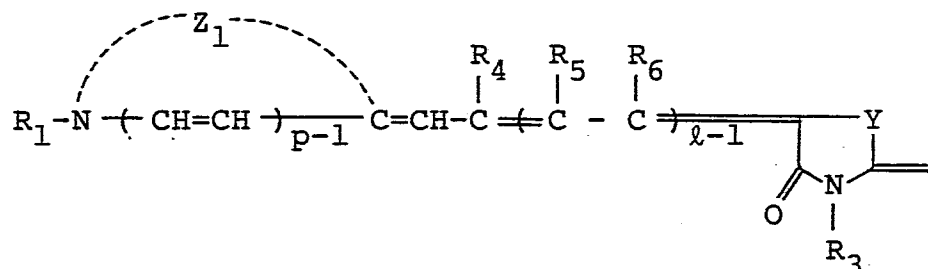
(II)



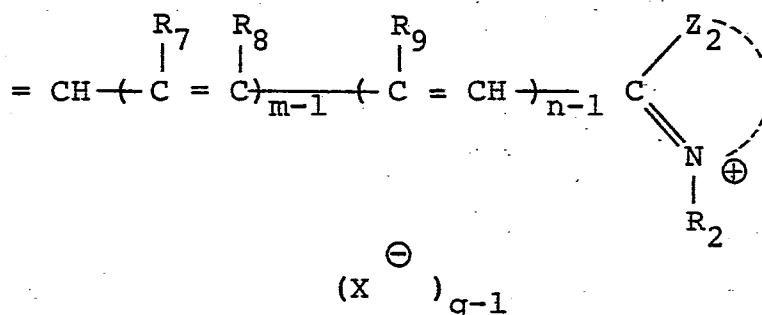
- 1 wherein X₁ and X₂ which may be identical or different represent oxygen atom, sulfur atom, selenium atom,
- 5 >N-R₇ (R₇ represents an alkyl group) or >C< $\begin{matrix} R_8 \\ R_9 \end{matrix}$ (R₈ and R₉ represent alkyl group); Z₁ and Z₂ which may be identical
- 10 or different represent a group of atoms necessary for forming a 5-membered nitrogen containing heterocyclic ring;
- 15 R₁ and R₂ which may be identical or different represent alkyl group, or alkenyl group; R₃ represents an alkyl group, an alkenyl group or an aryl group; R₄, R₅ and R₆ which may be identical or different represent hydrogen atom, halogen atom, alkyl group or aryl group; Y represents sulfur atom, oxygen atom or >N-R₁₀ (R₁₀ represents an alkyl group); Q represents a group of atoms necessary for forming a 5- or 6-membered ring by linking with carbon atom of methine chain; X represents an acid anion, and l, m and

1 q represent 1 or 2.

General formula (III):

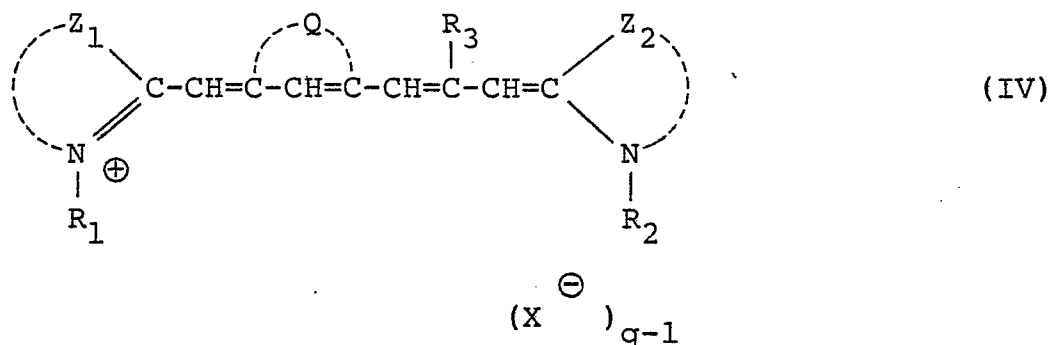


(III)



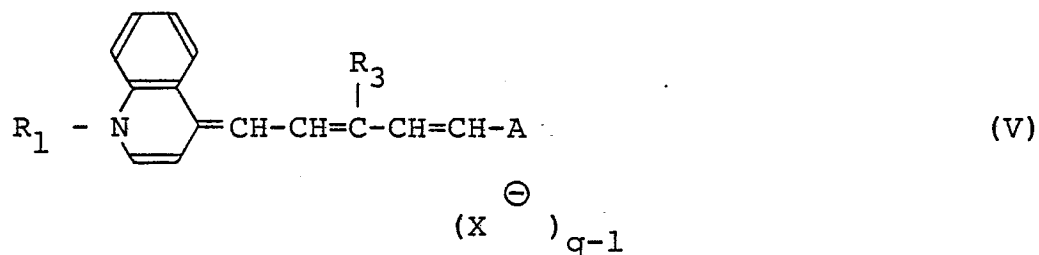
wherein Z₁ represents a group of atoms necessary for forming a 5- or 6-membered nitrogen containing heterocyclic ring; Z₂ represents a group of atoms necessary for forming a 5-membered nitrogen containing heterocyclic ring; R₁ and R₂ which may be identical or different represent alkyl group or alkenyl group; R₃ represents an alkyl group, an alkenyl group or an aryl group; R₄ - R₉ which may be identical or different represent hydrogen atom, halogen atom, alkyl group or aryl group; Y represents sulfur atom, oxygen atom, halogen atom, alkyl group or aryl group; Y represents sulfur atom, oxygen atom, or >N-R₁₀ (R₁₀ represents an alkyl group); X represents an acid anion; l, m, n, p and q represent 1 or 2 with a proviso that when m and n are both 1, l is 2.

General formula (IV):

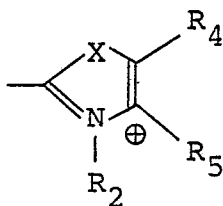


- 1 wherein Z_1 and Z_2 which are different represent thiazole ring, selenazole ring or oxazole ring which may have a condensed ring; R_1 and R_2 which may be identical or different represent alkyl group or alkenyl group; R_3 represents
- 5 hydrogen atom, an alkyl group or an aryl group; Q represents a group of atoms necessary for forming a 5- or 6-membered ring by linking with carbon atom of methine chain; X represents an acid anion; and Q represents 1 or 2.

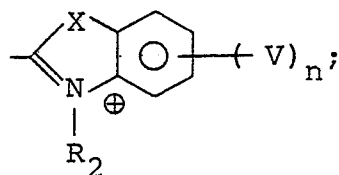
General formula (V):



wherein A represents



or



1 X represents sulfur atom, selenium atom, oxygen atom or
 >N-R₆ (R₆ represents an alkyl group); R₄ and R₅ represent
 hydrogen atom, alkyl group or aryl group with a proviso
 that R₄ and R₅ cannot be both hydrogen atoms; V represents
 5 an alkyl group, an alkoxy group, an aryl group, an alkoxy-
 carbonyl group, an alkenyl group, a carboxy group, hydroxy
 group or a halogen atom; n represents 0 or an integer of
 1 - 4 and when n is 0, V forms naphthothiazole ring; R₁
 and R₂ represent alkyl group or alkenyl group; R₃ re-
 10 presents hydrogen atom, an alkyl group or an aryl group;
 X represents an acid anion; and q represents 1 or 2.

The sensitizing dyes represented by the general
 formula (I) and those represented by the general formula (II)
 are rhodacyanine dyes, characterized by having the -OR₇ group
 15 and the ring Q, respectively and they exhibit the best
 results among the dyes used in this invention.

As examples of Z₁ and Z₂ in the general formula
 (I), mention may be made of nitrogen containing heterocyclic
 rings such as thiazole, benzothiazole, naphtho[1,2-d]
 20 thiazole, naphtho[2,1-d]thiazole, naphtho[2,3-d]thiazole,
 selenazole, benzoselenazole, naphtho[2,1-d]selenazole,
 naphtho[1,2-d]selenazole, oxazole, benzoxazole, naphtho
 [1,2-d]oxazole, naphtho[2,1-d]oxazole, naphtho[2,3-d]oxazole,
 2-quinoline, 4-quinoline, 3,3-dialkylindolenine, imidazole,
 25 benzimidazole, naphtho[1,2-d]imidazole, pyridine, etc. These
 heterocyclic rings may have one or more substituents such as
 alkyl groups (e.g., methyl, ethyl, butyl, trifluoromethyl,
 etc.), aryl groups (e.g., phenyl, tolyl, etc.), hydroxy

1 group, alkoxy groups (e.g., methoxy, ethoxy, butoxy, etc.),
carboxy group, alkoxycarbonyl groups (e.g., methoxycarbonyl,
ethoxycarbonyl, etc.), halogen atoms (e.g., fluorine, chlo-
rine, bromine and iodine), aralkyl groups (e.g., benzyl,
5 phenethyl, etc.), cyano group, alkenyl groups (e.g., allyl,
etc.), etc.

For R_1 , R_2 and R_7 , examples of alkyl group are
lower alkyl groups such as methyl, ethyl, propyl, butyl,
etc.; hydroxyalkyl groups such as β -hydroxyethyl, γ -hydroxy-
10 propyl, etc.; alkoxyalkyl groups such as β -methoxyethyl, γ -
methoxypropyl, etc.; acyloxyalkyl groups such as β -acetox-
ethyl, γ -acetoxypentyl, β -benzoyloxyethyl, etc.; carboxyalkyl
groups such as carboxymethyl, β -carboxyethyl, etc.; alkoxy-
carbonylalkyl groups such as methoxycarbonylmethyl, ethoxy-
15 carbonylmethyl, β -ethoxycarbonylethyl, etc.; sulfoalkyl
groups such as β -sulfoethyl, γ -sulfopropyl, δ -sulfobutyl,
etc.; aralkyl groups such as benzyl, phenethyl, sulfobenzyl,
etc. and examples of alkenyl group are allyl, etc.

As examples of R_3 , mention may be made of alkyl
20 and alkenyl groups as enumerated for the above R_1 and R_2 and
phenyl, tolyl, methoxyphenyl, chlorophenyl, naphthyl, etc.
as aryl groups.

For $R_4 - R_6$, examples of alkyl and aryl groups
are those enumerated for the above R_1 and R_2 and 5- or
25 6-membered rings formed with R_4 and R_6 may be substituted
with a lower alkyl group or the like. Examples of R_8 are
alkyl groups as enumerated for R_1 and R_2 .

Examples of acid anion of X are alkylsulfate ions

1 such as methylsulfuric acid, ethylsulfuric acid, etc., thio-
cyanate ion, toluenesulfonate ion, halogen ions such as
chlorine, bromine, iodine, etc., perchlorate ions, etc. When
the dyes have betaine analogous structure, X is absent.

5 l is 0 or 1 and m, n and q are 1 or 2.

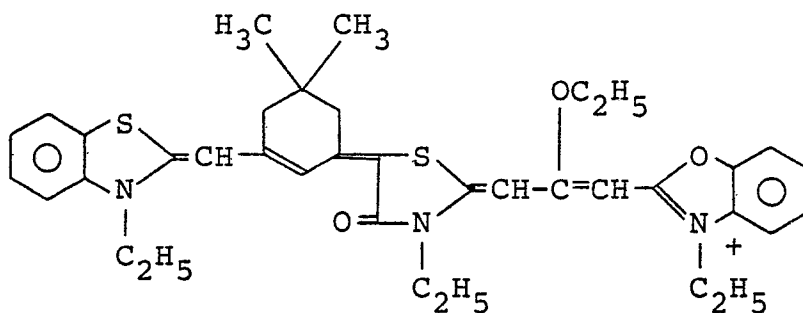
In the general formula (II), as examples of Z_1 and
 Z_2 , mention may be made of the 5-membered nitrogen containing
heterocyclic rings enumerated as examples of Z_1 and Z_2 of the
general formula (I) and these heterocyclic rings may have
10 such substituents as those of Z_1 and Z_2 of the general
formula (I). As examples of $R_1 - R_3$, mention may be made of
such alkyl groups, alkenyl groups and aryl groups as enume-
rated as examples of $R_1 - R_3$ of the general formula (I). As
examples of the alkyl and aryl groups of $R_4 - R_6$, mention may
15 be made of such groups as enumerated as examples of the above
 R_1 and R_2 and as examples of halogen atoms, mention may be
made of fluorine, chlorine, bromine and iodine. Examples of
alkyl group of $R_7 - R_{10}$ are lower alkyl groups such as
methyl, ethyl, etc. The ring represented by Q may be sub-
20 stituted with a lower alkyl group such as methyl group, etc.
X is such acid anion as enumerated as examples of X of the
general formula (I).

As examples of symbols in the general formulas
(III) - (V), mention may be made of those enumerated as ex-
25 amples of those in the general formulas (I) and (II) within
the scope of definitions in the general formulas (III) - (V).

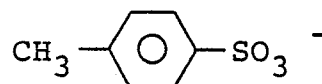
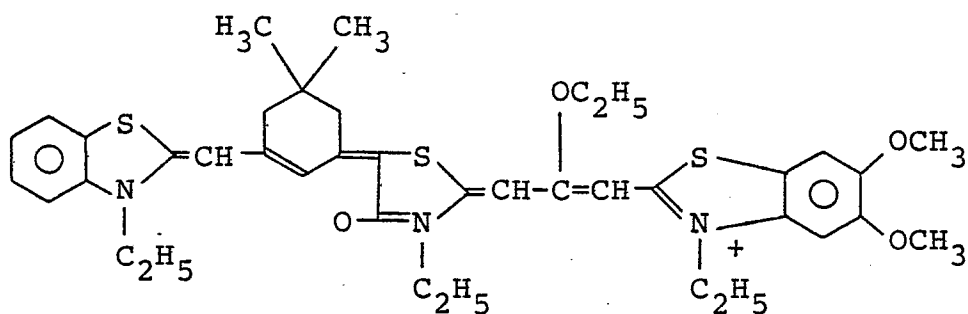
Typical examples of the sensitizing dyes used in
this invention are shown below.

Examples of the sensitizing dyes represented by the general formula (I).

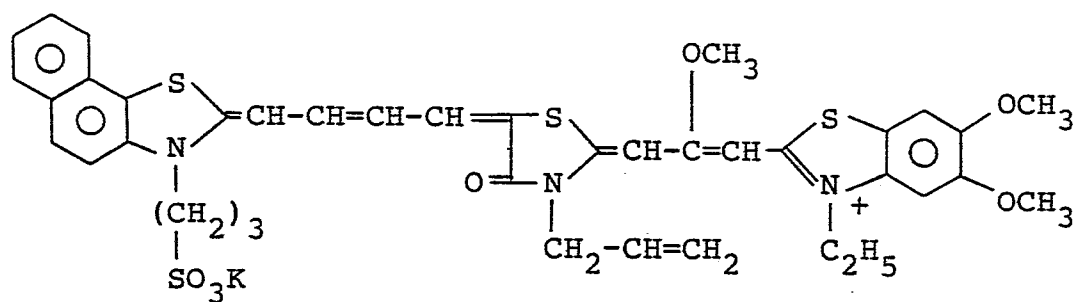
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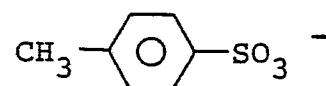
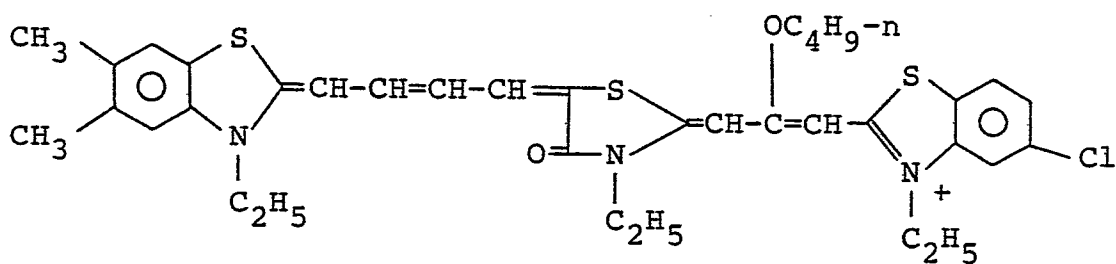
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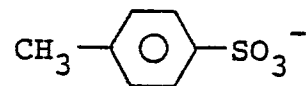
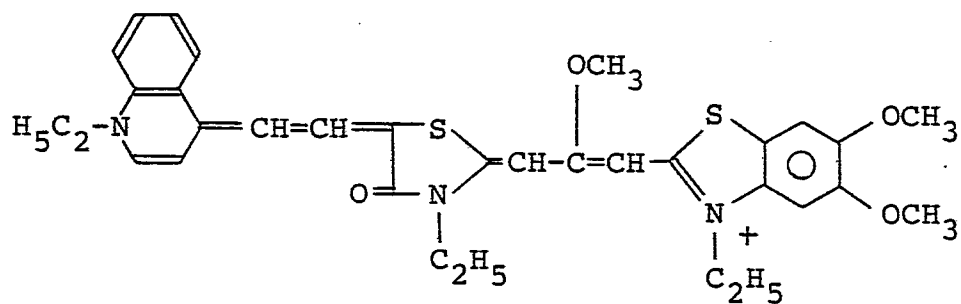
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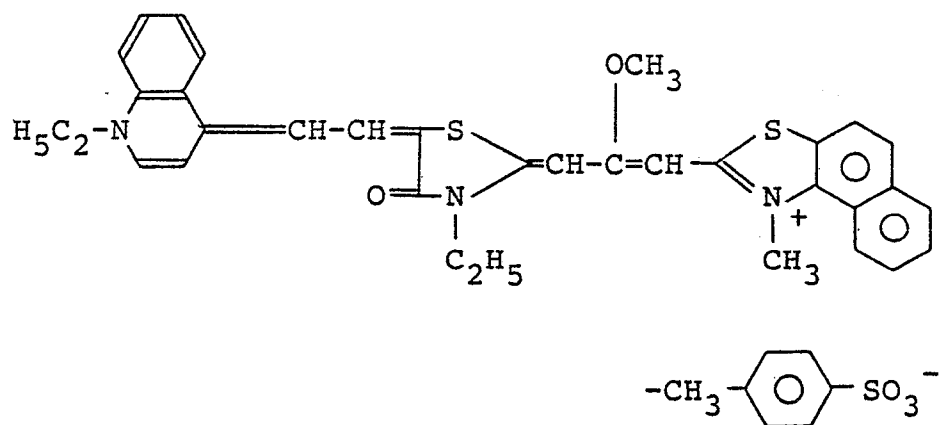
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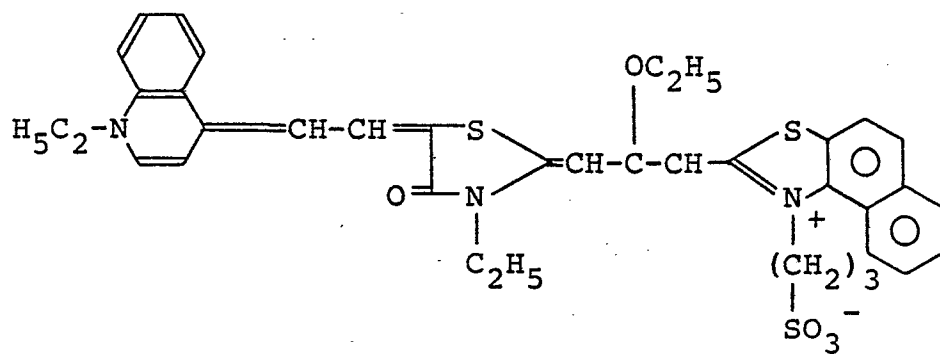
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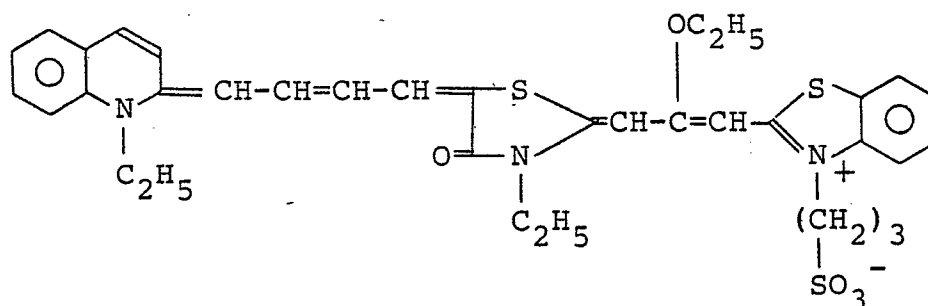
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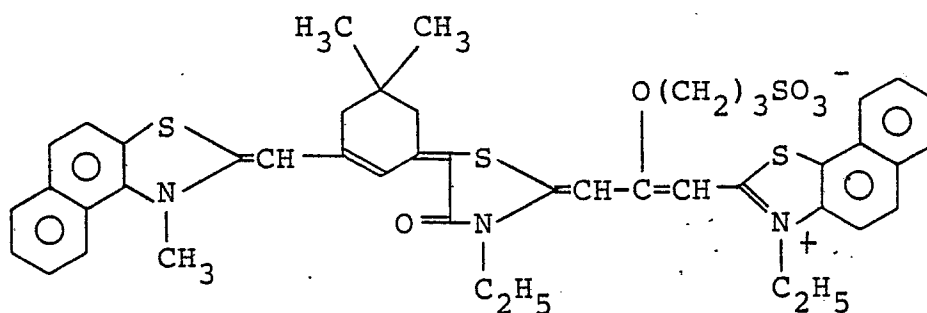
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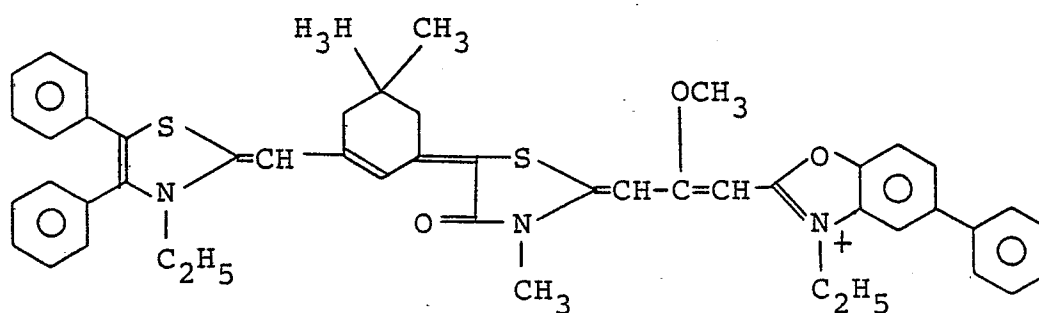
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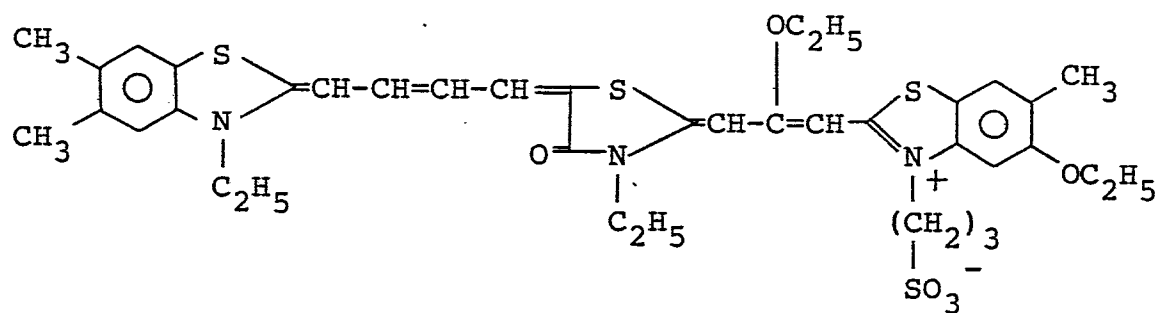
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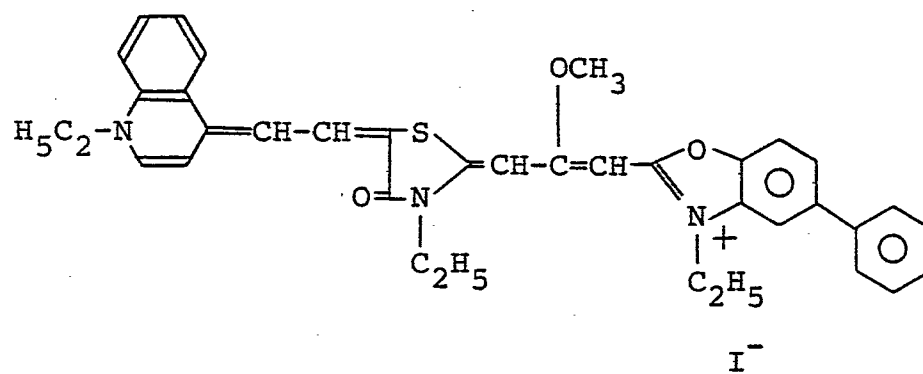
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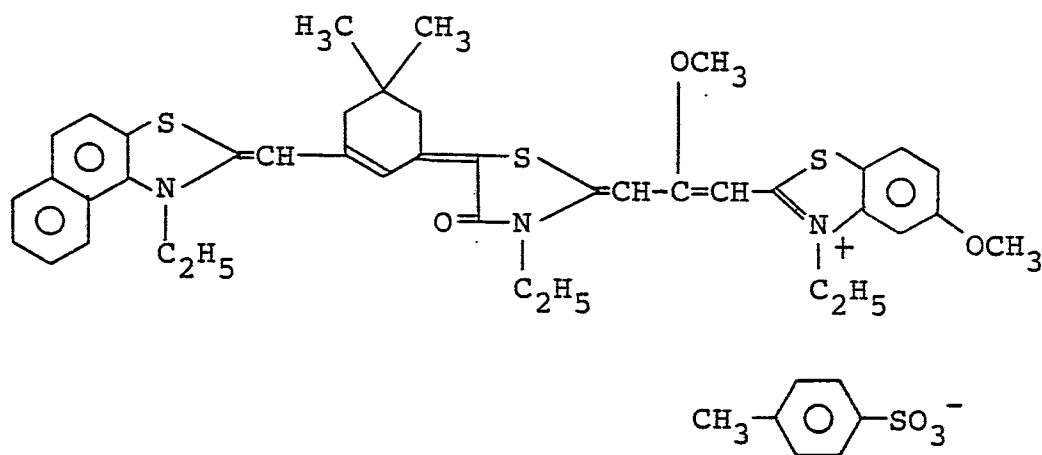
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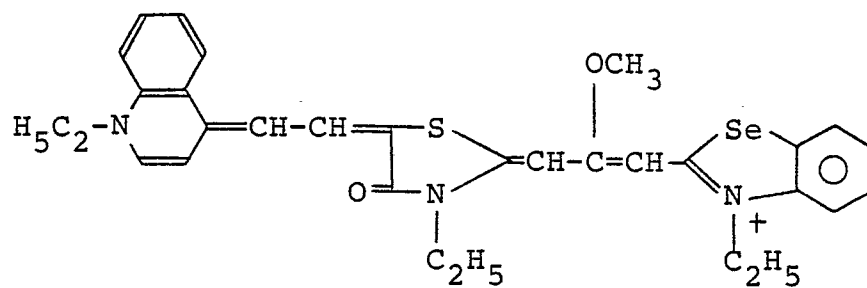
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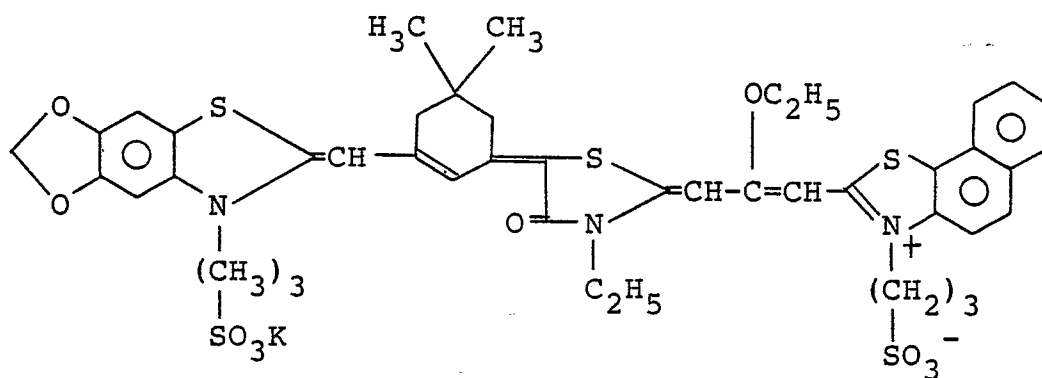
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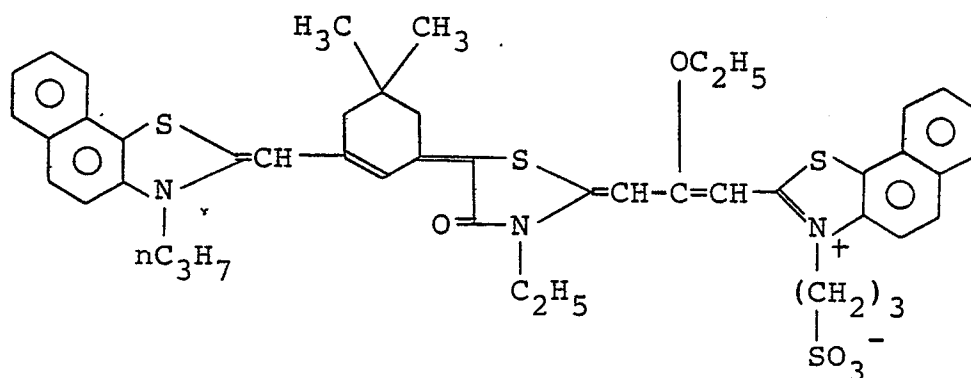
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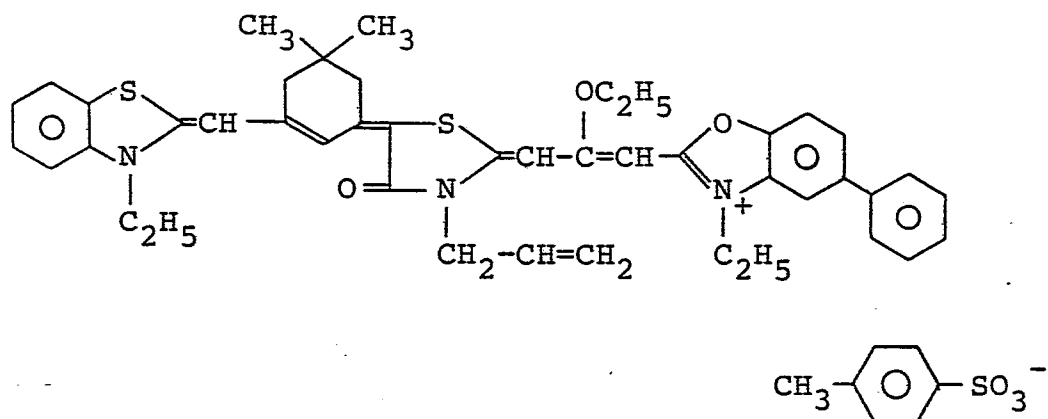
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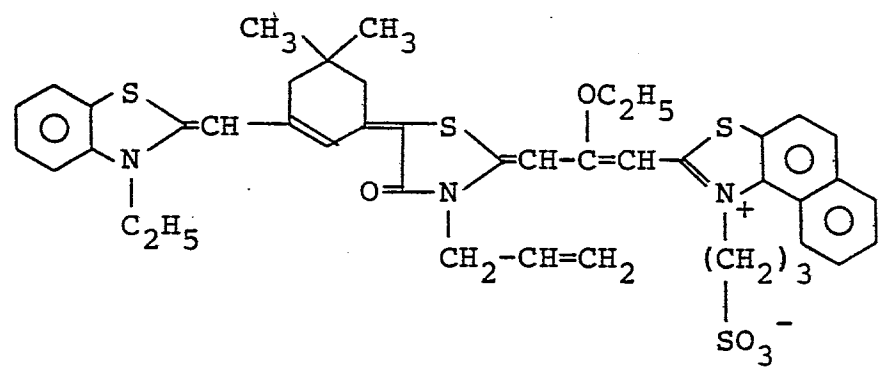
[I-19]



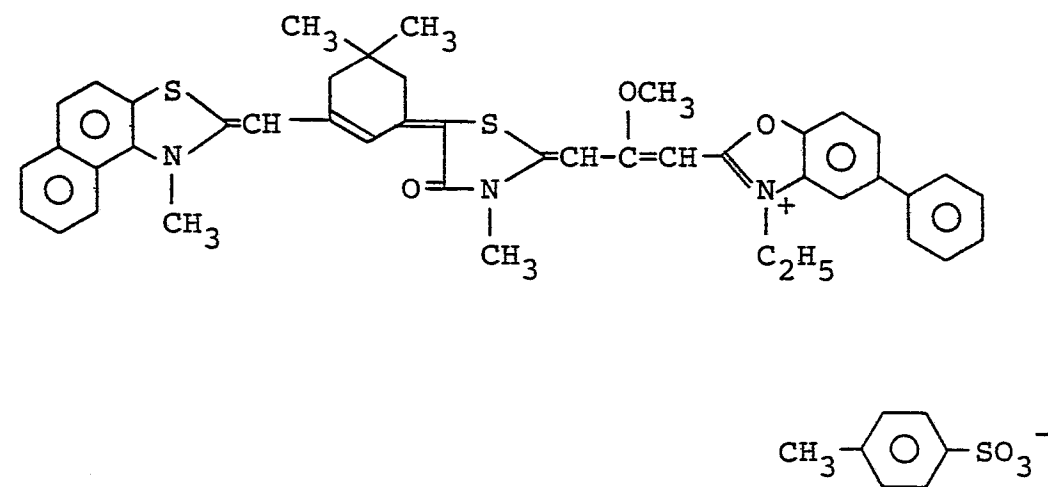
[I-20]



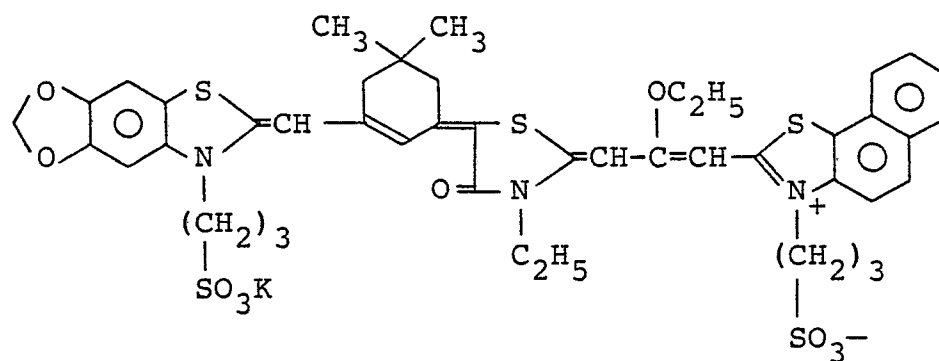
[I-21]



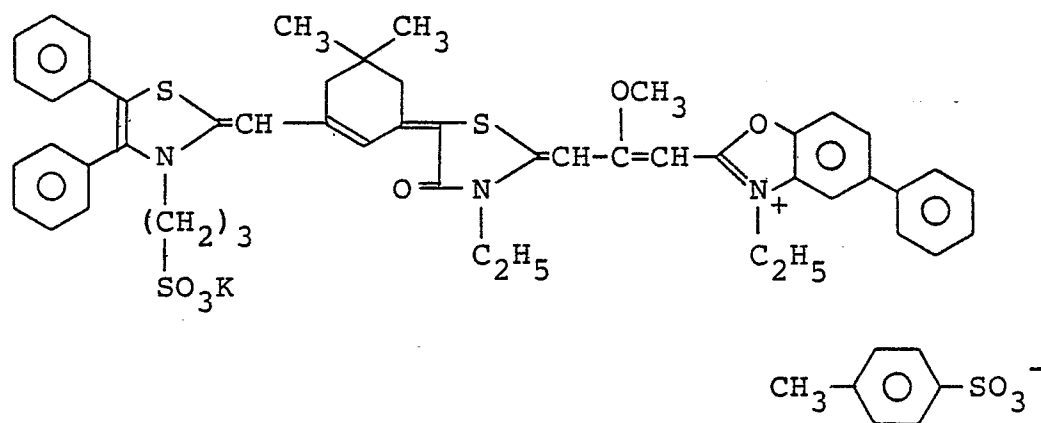
[I-22]



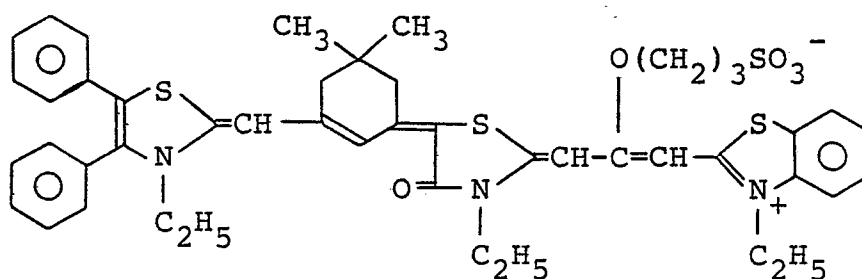
[I-23]



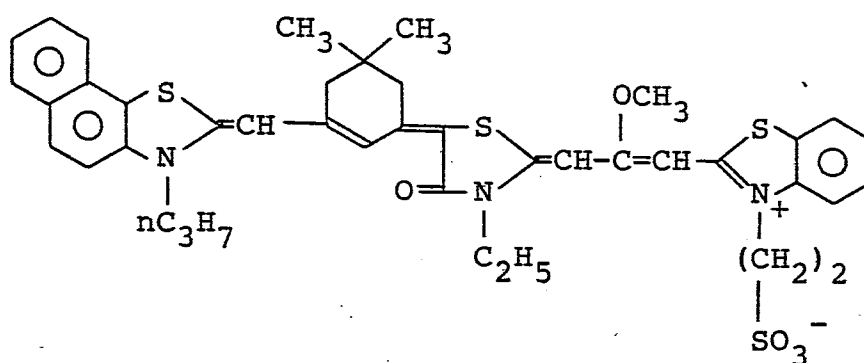
[I-24]



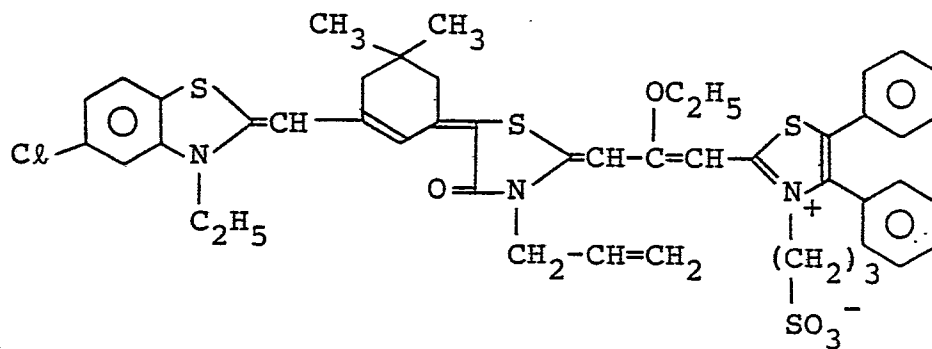
[I-25]



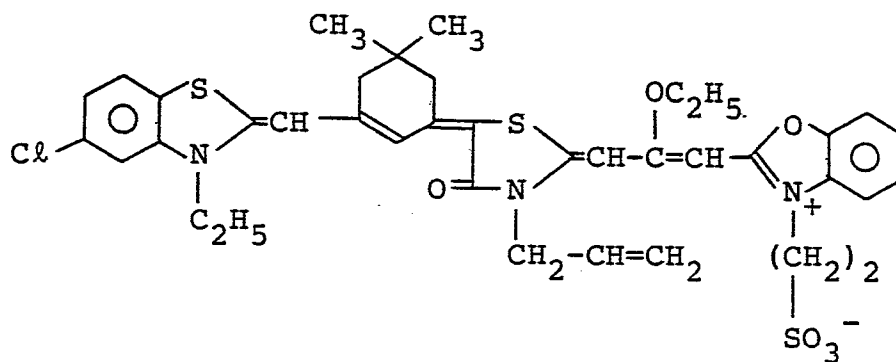
[I-26]



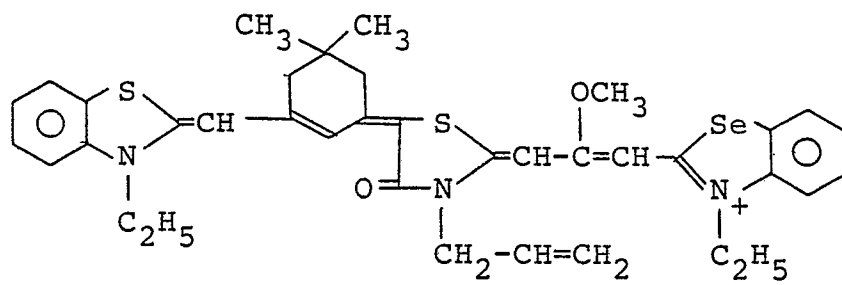
[I-27]



[I-28]

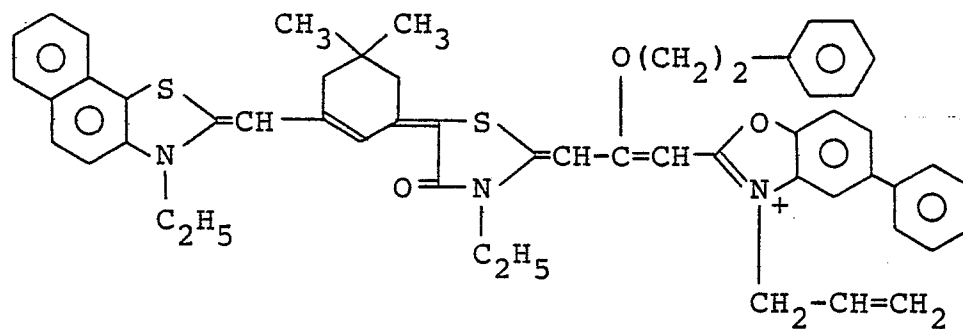


[I-29]



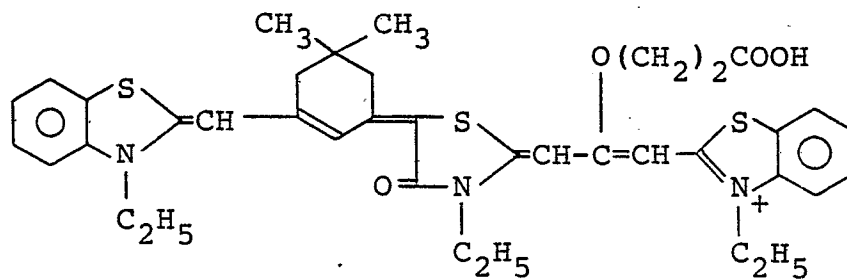
I⁻

[I-30]



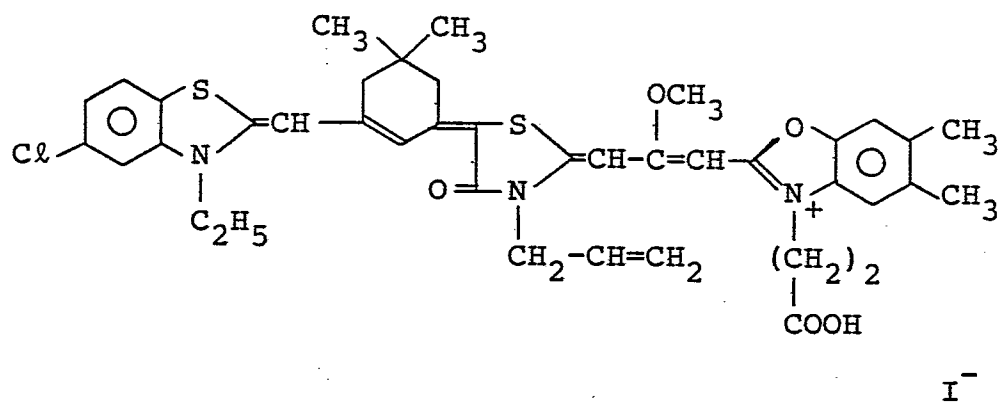
I⁻

[I-31]

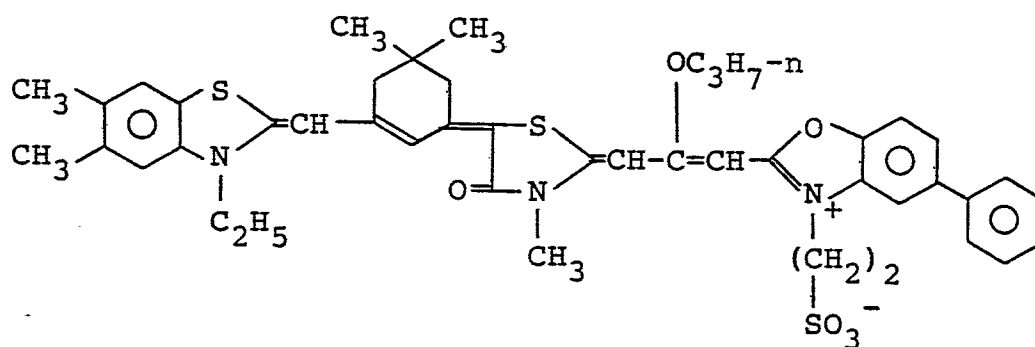


I⁻

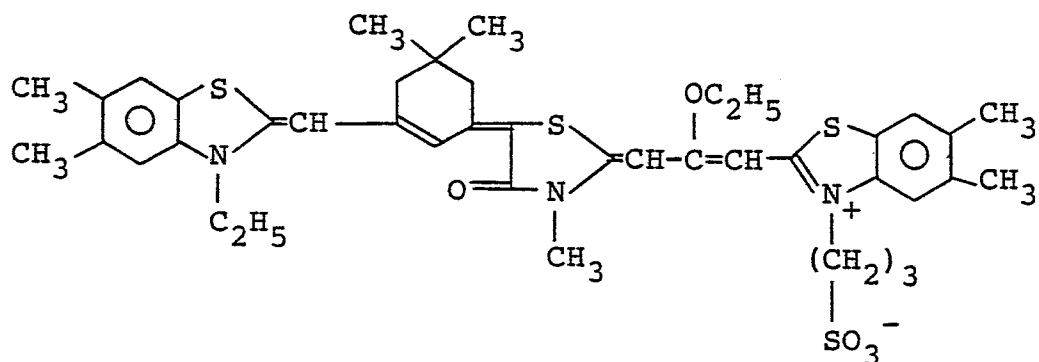
[I-32]



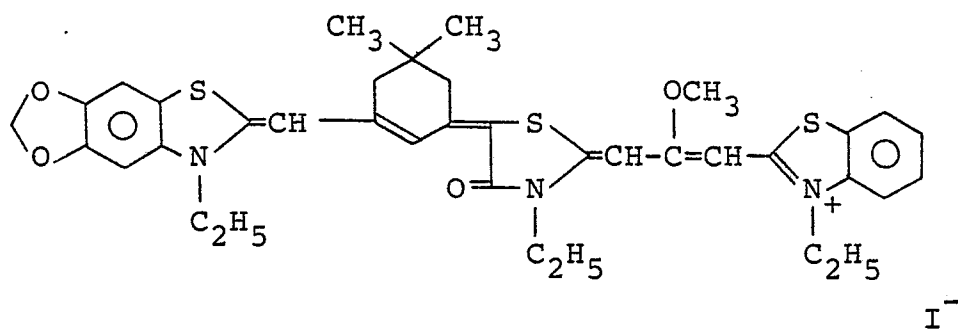
[I-33]



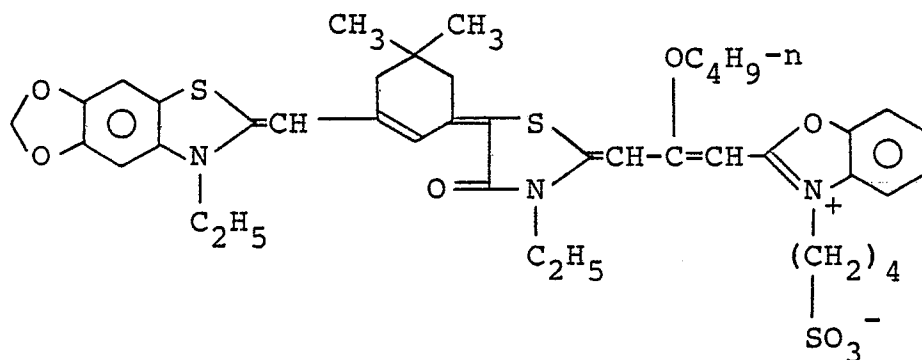
[I-34]



[I-35]

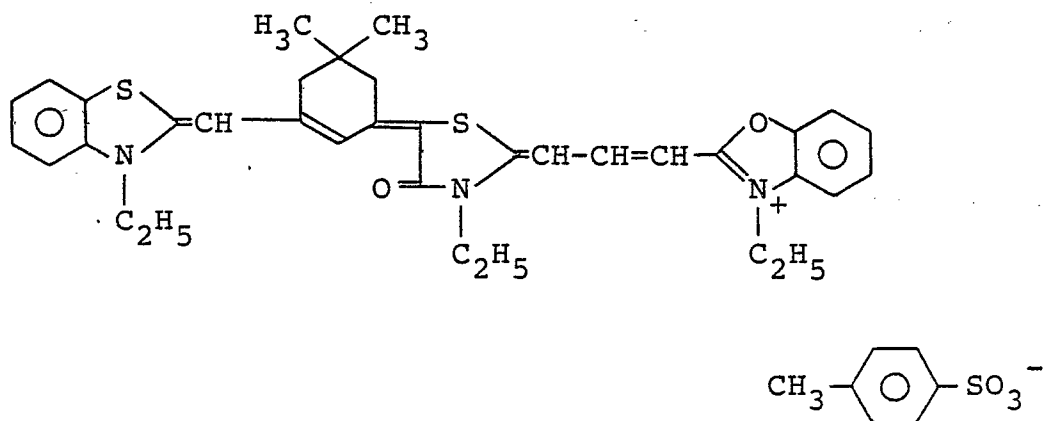


[I-36]

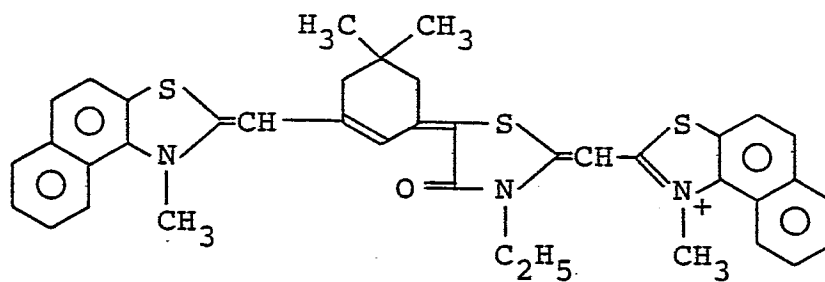


Examples of the sensitizing dyes represented by the general formula (II).

[II-1]

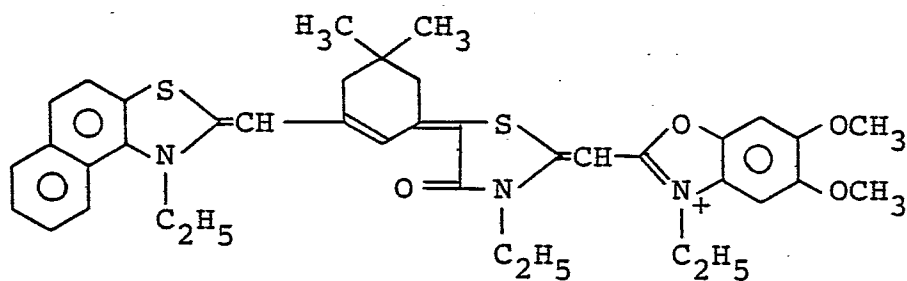


[II-2]



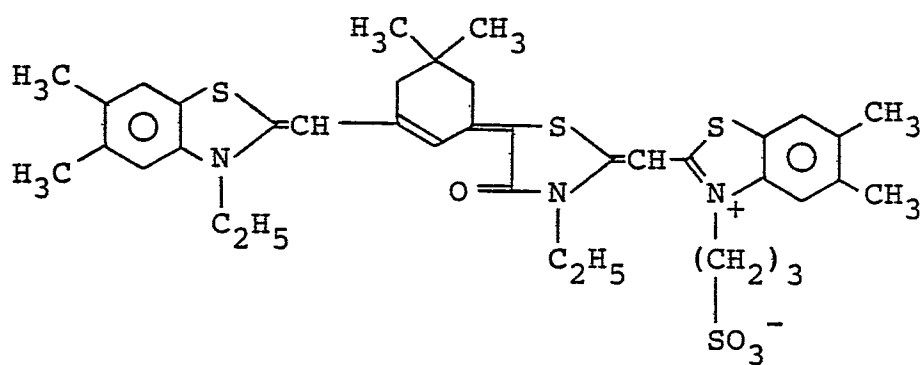
I⁻

[II-3]

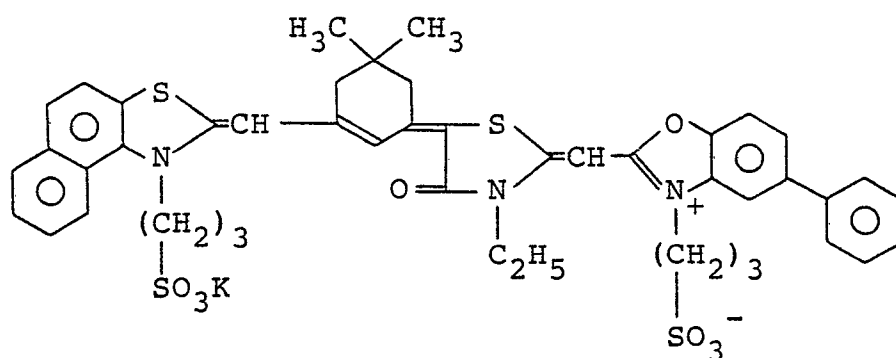


I⁻

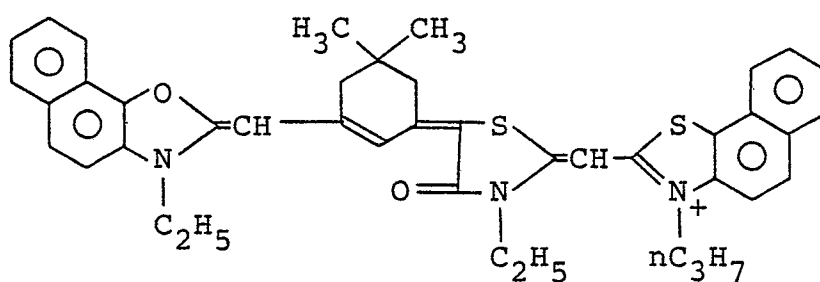
[II-4]



[II-5]

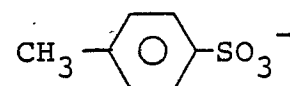
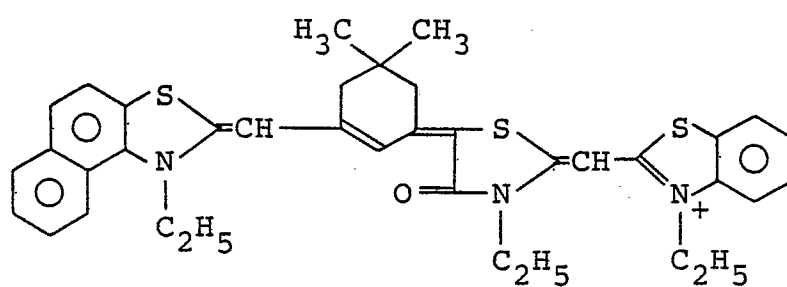


[II-6]

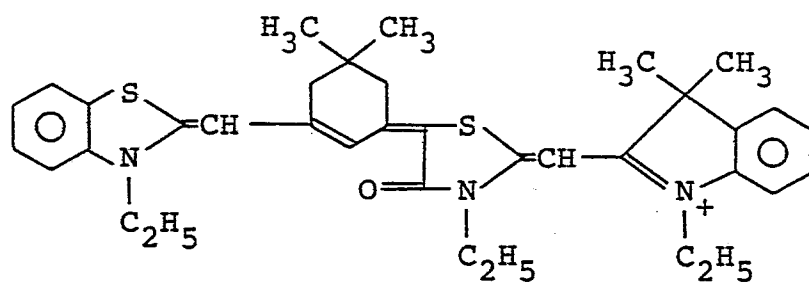


I⁻

[II-7]

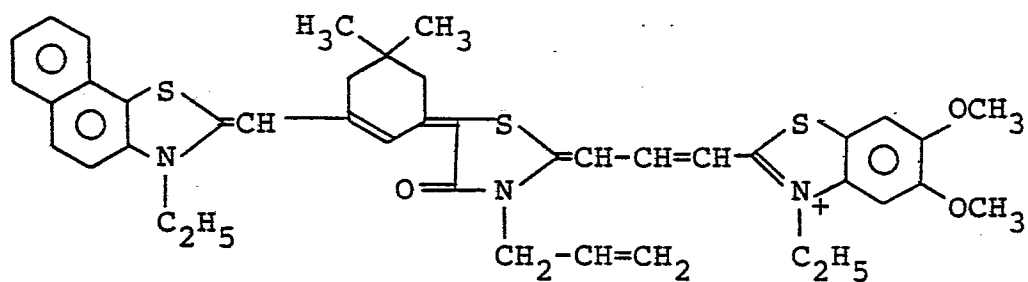


[II-8]



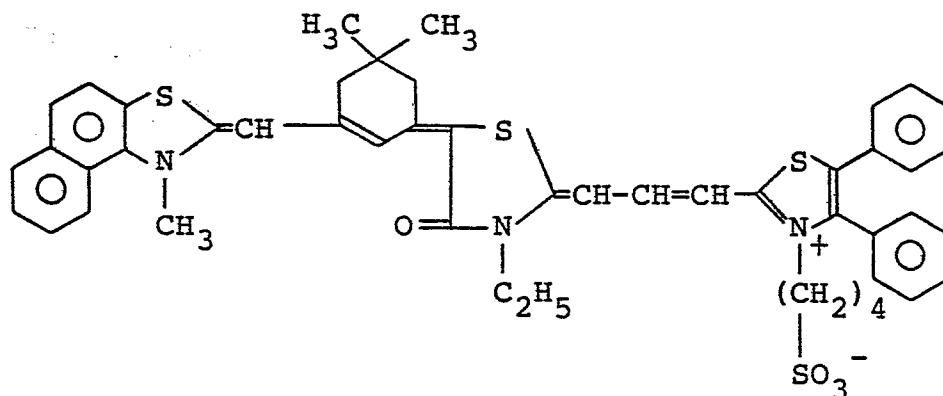
I⁻

[II-9]

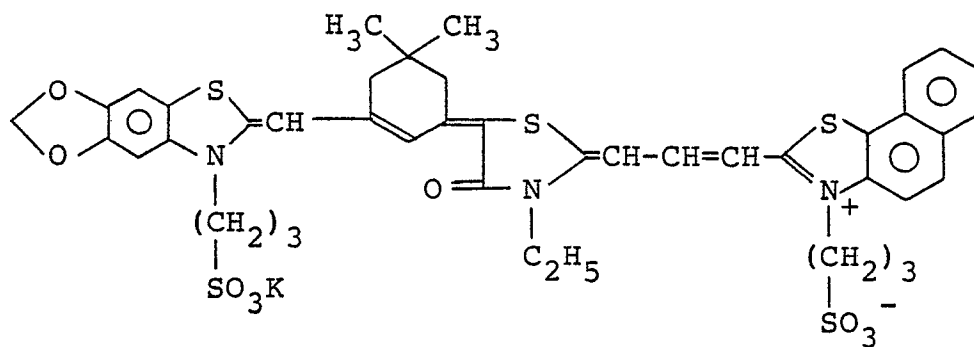


I⁻

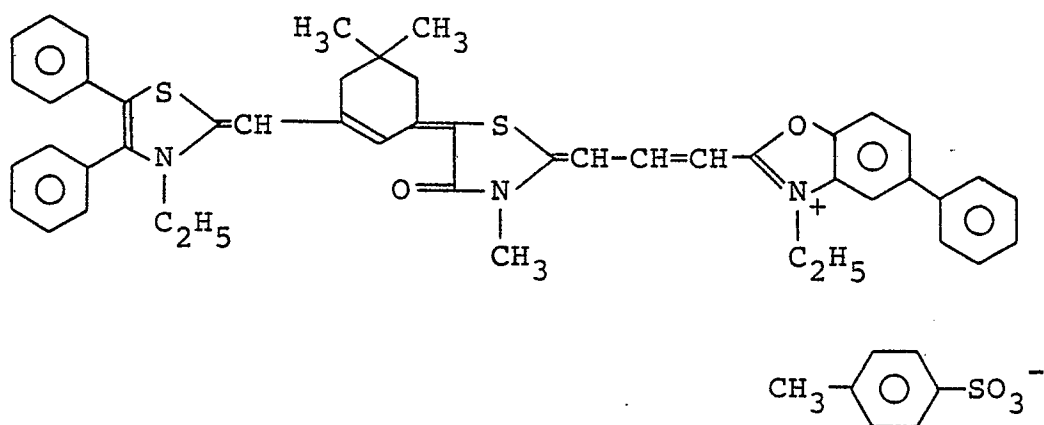
[II-10]



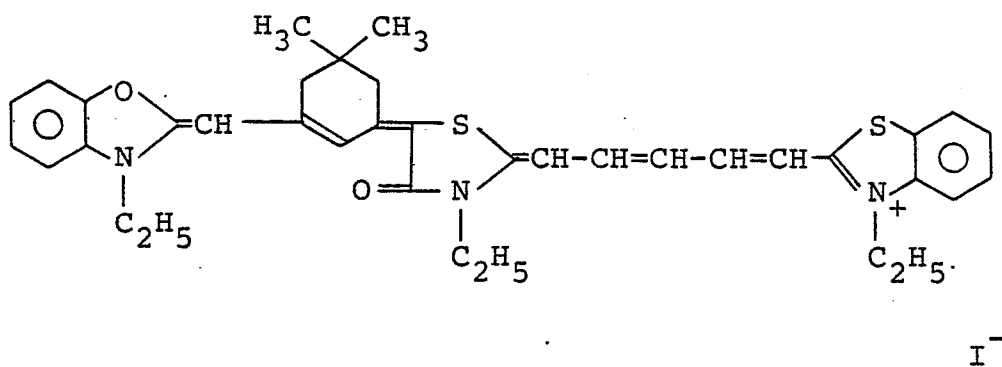
[II-11]



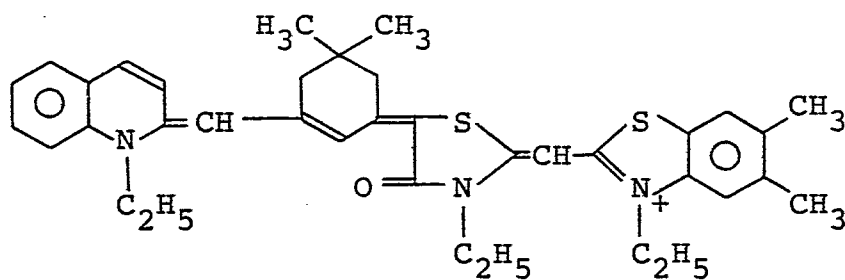
[II-12]



[II-13]



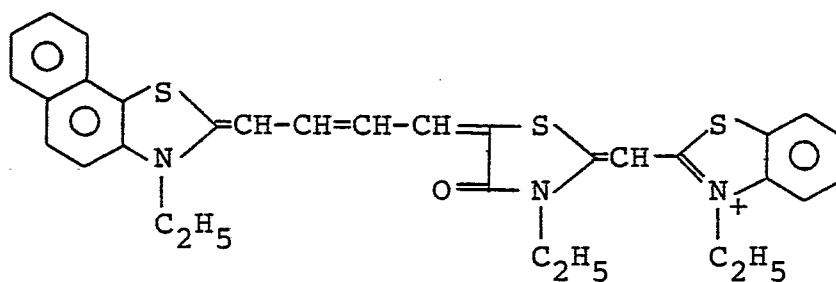
[II-14]



I⁻

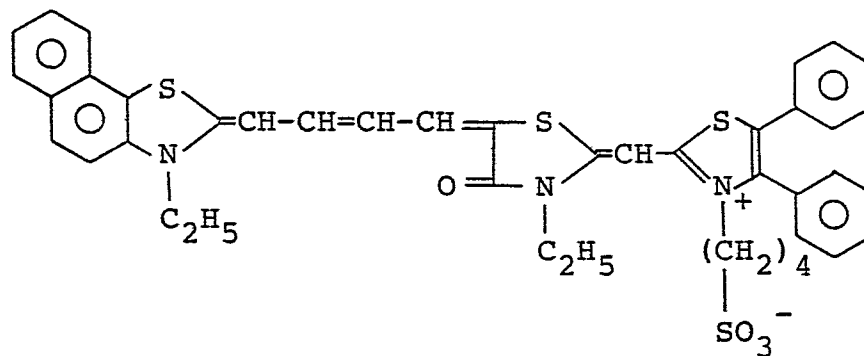
Examples of the sensitizing dyes represented by the general formula (III).

[III-1]

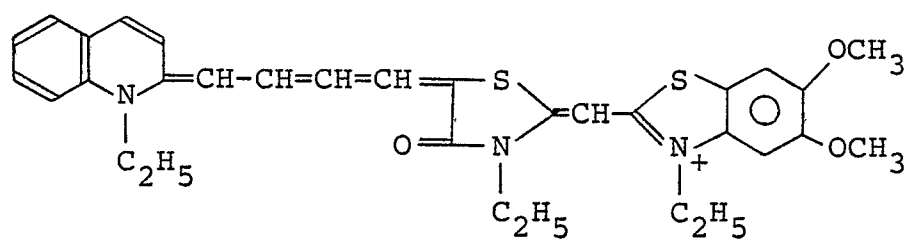


I⁻

[III-2]

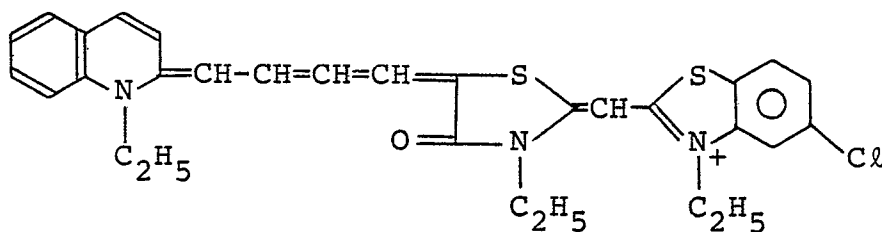


[III-3]



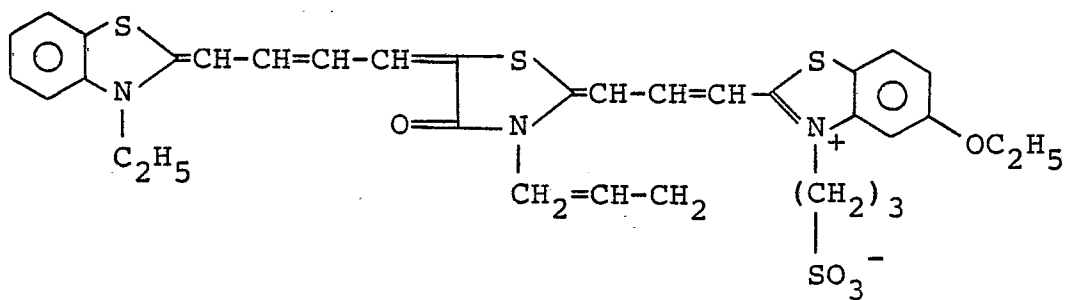
I⁻

[III-4]

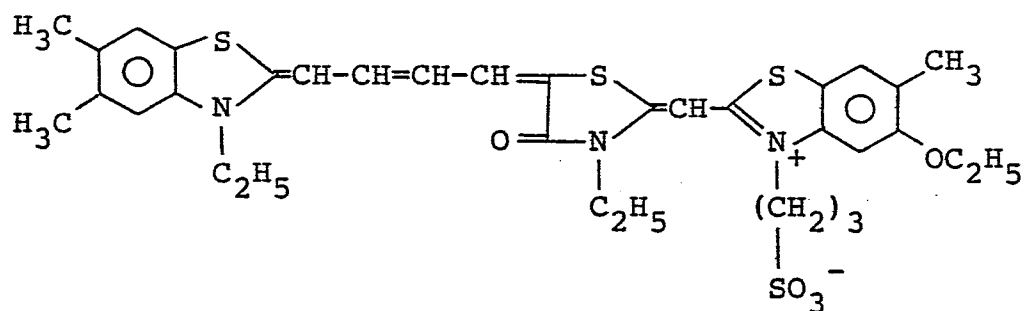


I⁻

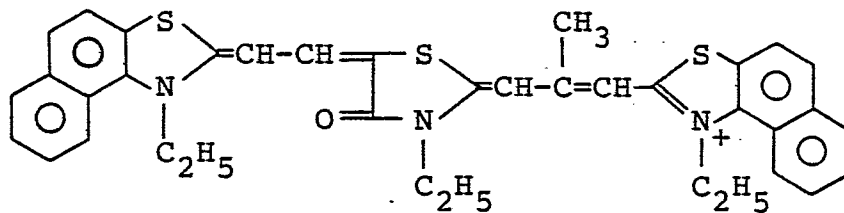
[III-5]



[III-6]

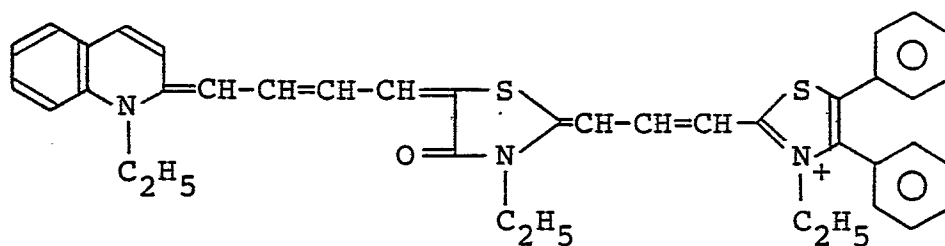


[III-7]



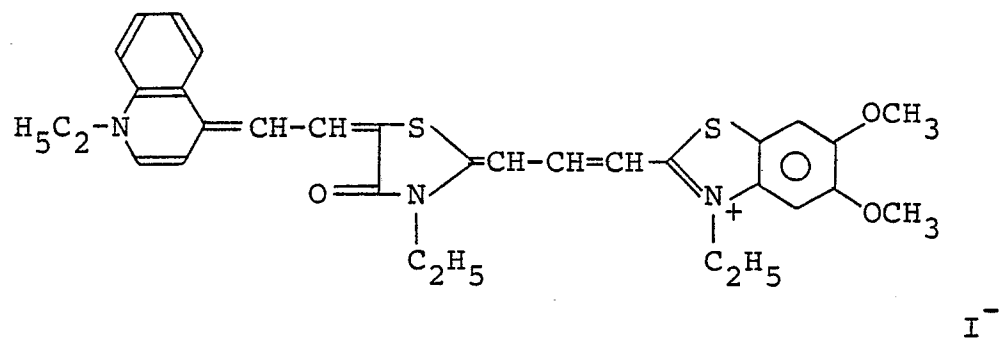
I-

[III-8]

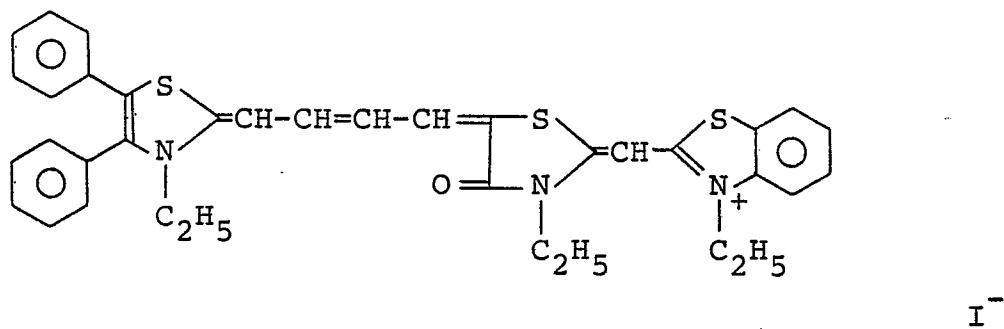


I-

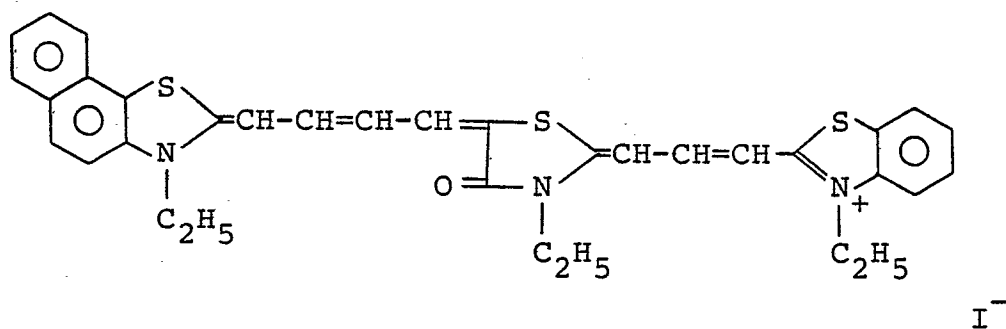
[III-9]



[III-10]

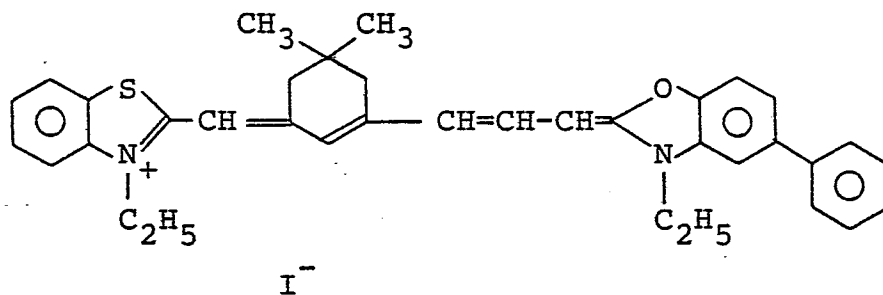


[III-11]

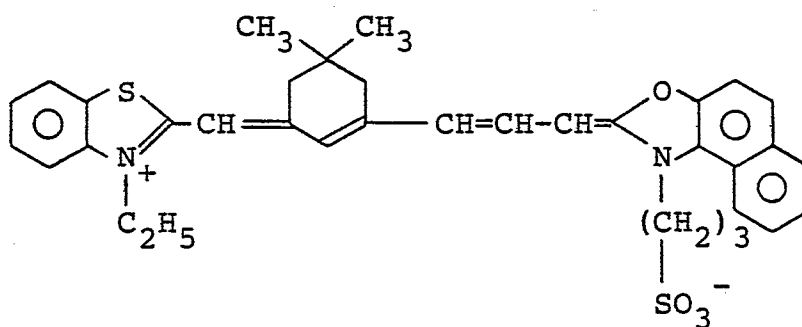


- 1 Examples of the sensitizing dyes represented by the general formula (IV)

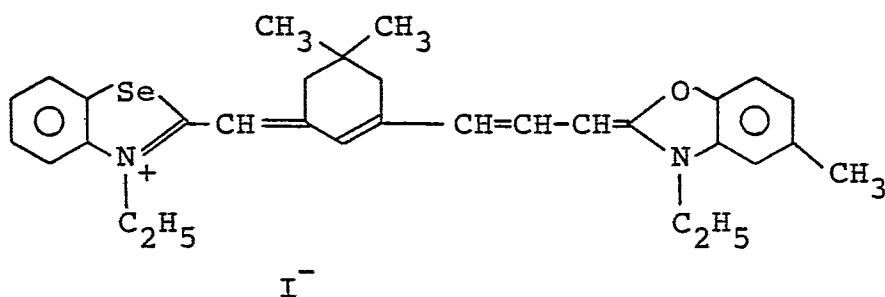
[IV-1]



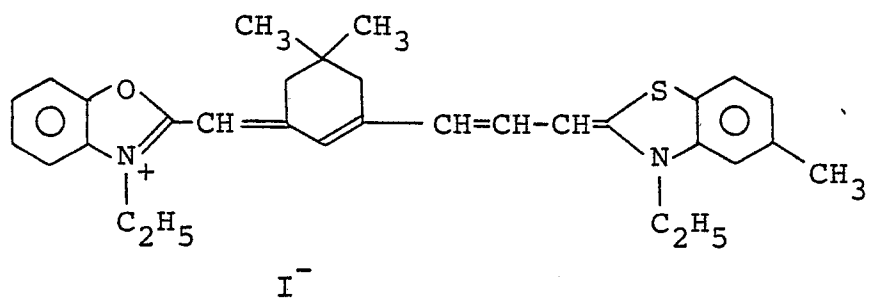
[IV-2]



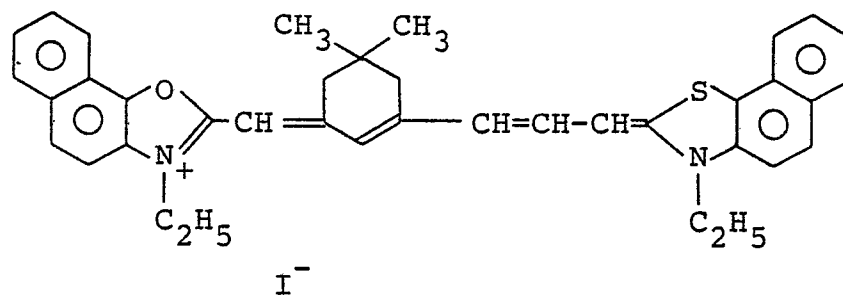
[IV-3]



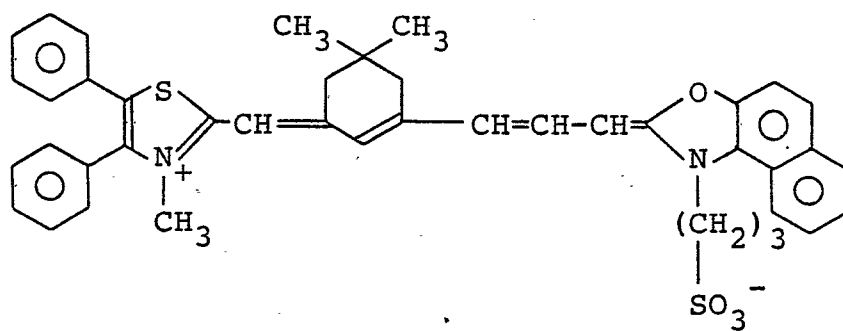
[IV-4]



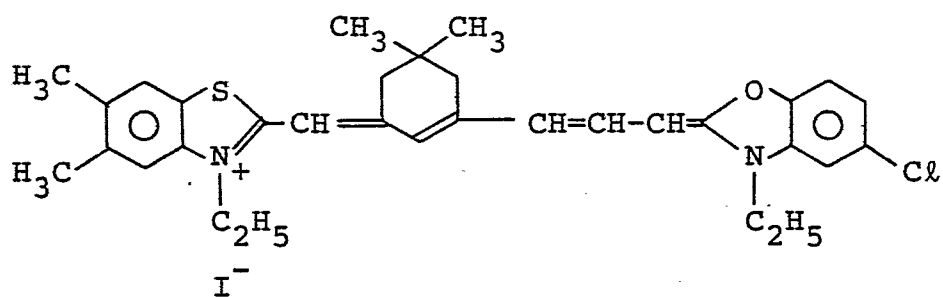
[IV-5]



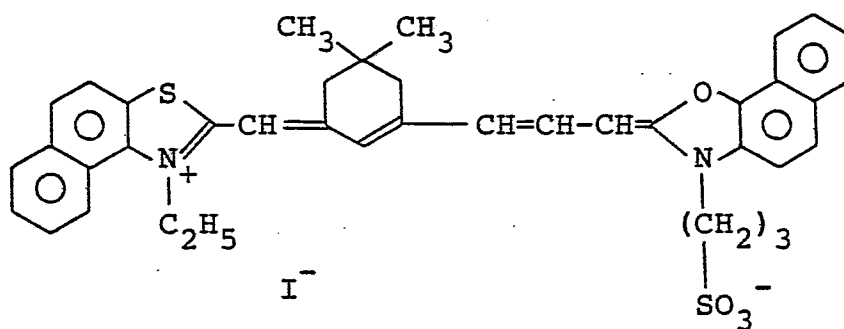
[IV-6]



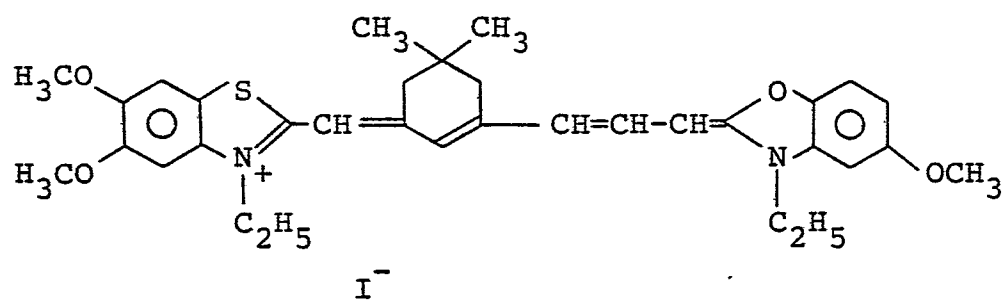
[IV-7]



[IV-8]

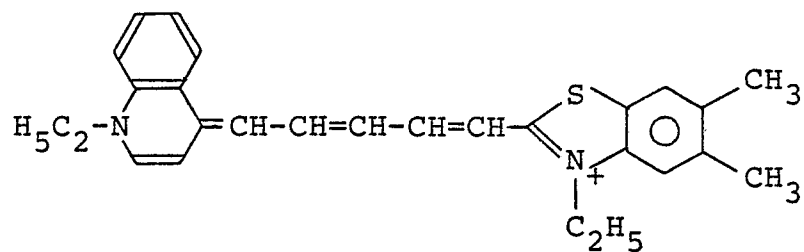


[IV-9]



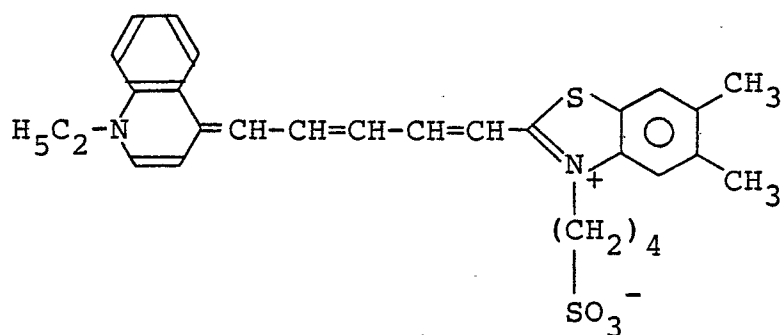
- 1 Examples of the sensitizing dyes represented by the general formula (V).

[V-1]

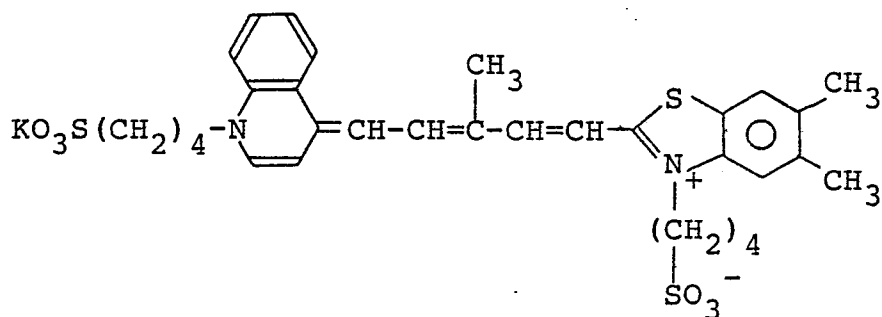


I⁻

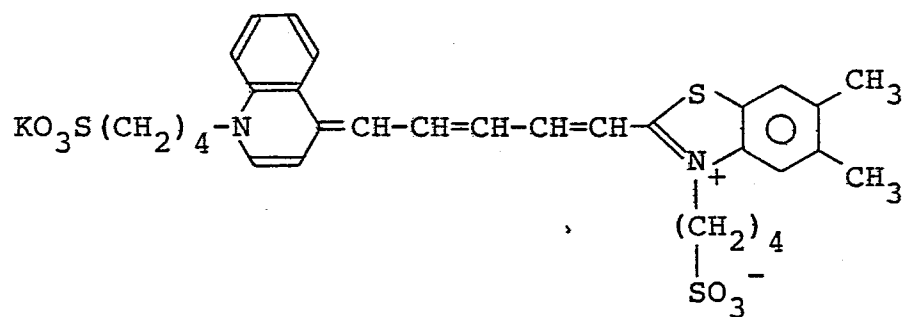
[V-2]



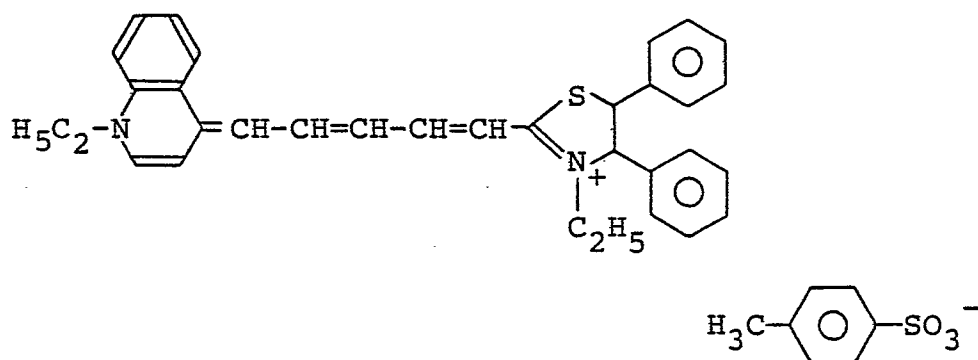
[V-3]



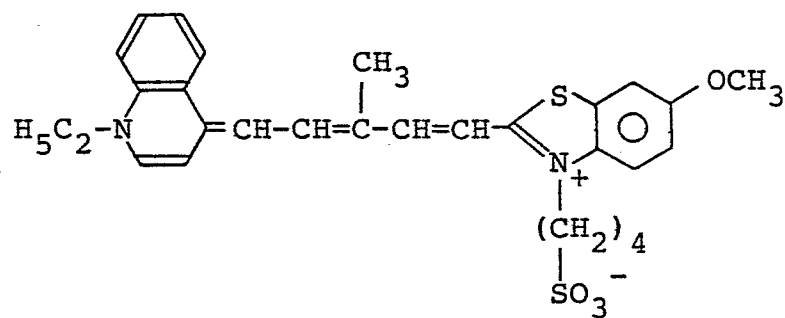
[V-4]



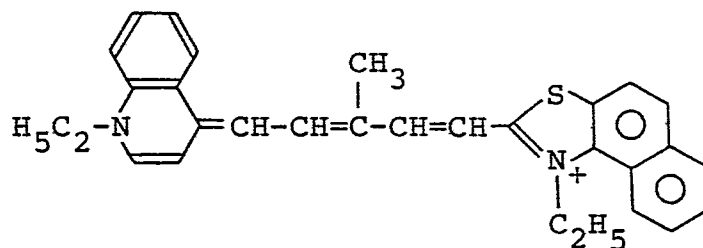
[V-5]



[V-6]

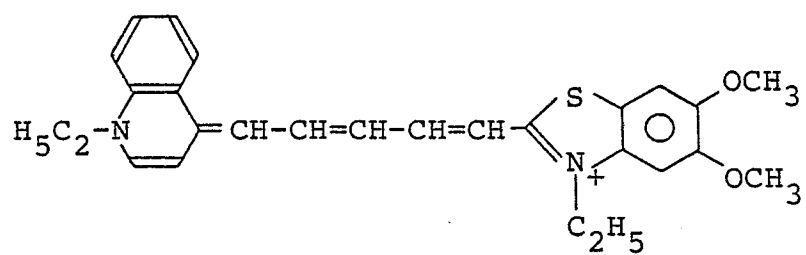


[V-7]



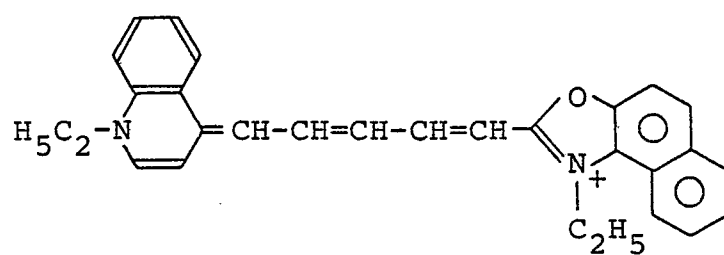
I⁻

[V-8]



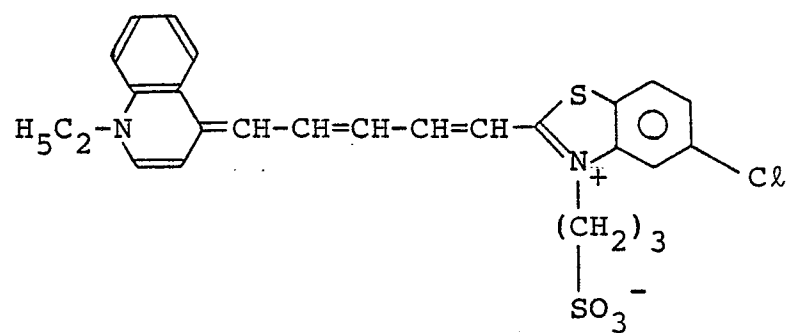
I⁻

[V-9]

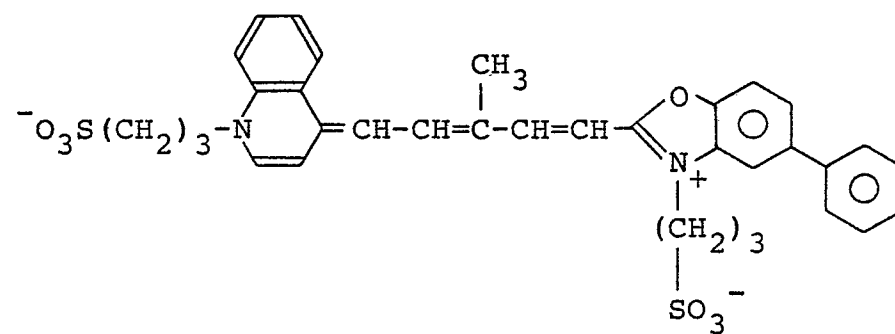


I⁻

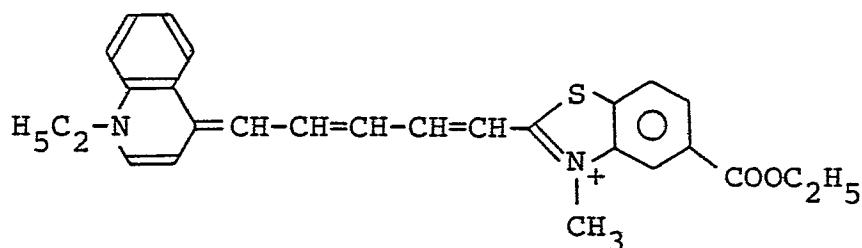
[V-10]



[V-11]

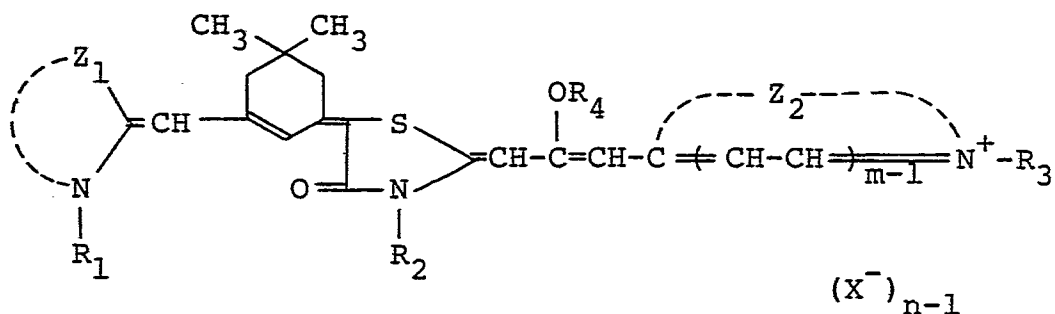


[V-12]



1 This invention also includes photographic light sensitive materials having a silver halide emulsion layer which contains a novel rhodacyanine dye represented by the following general formula (VI).

General formula (VI)



5 wherein Z₁ represents a group of atoms necessary for forming a thiazole ring, benzothiazole ring or naphtho-
thiazole ring; Z₂ represents a group of atoms necessary for
forming a 5- or 6-membered nitrogen containing hetero-
cyclic ring; R₁, R₃ and R₄ represent alkyl group, aralkyl
10 group or alkenyl group; R₂ represents an alkyl group, an
aralkyl group, an alkenyl group or an aryl group; X repre-
sents an acid anion; and m and n represent 1 or 2.

1 Examples of these dyes are shown as examples of
the dyes represented by the general formula (I).

Typical example of synthesis of the novel
rhodacyanine dye used in this invention is shown below.

5 Synthesis of dye [I-10]:

2.21 g of 3-ethyl-5-[3-(3-ethylbenzothiazoline-
2-ylidene)methyl-5,5-dimethyl-2-cyclohexene-1-ylidene]
rhodanine (disclosed in U.S. Patent 2,856,404) was mixed
with 3.15 g of dimethylsulfuric acid and the mixture was
10 heated to a bath temperature of 90-100°C for 15 minutes.
After cooling, the reaction product was washed with ethyl
ether, followed by adding 2.16 g of 2-(2-ethoxy-1-
propenyl)-3-ethyl-5,6-dimethylbenzoxazolium-p-toluene-
sulfonate and 30 ml of ethanol and heating to obtain a homo-
15 geneous solution. Then, 3.0 ml of triethylamine was added
to the solution, which was then subjected to reflux for
30 minutes with heating. After termination of the reac-
tion, ethyl acetate was added thereto and the precipitate
was filtered off and washed with ethyl acetate. The
20 resulting crude dye was recrystallized twice with ethanol
and dried to give 1.00 g of dark yellowish green crystalline
powder having a melting point of 197.0°C (dec.).
Absorption maximum of methanolic solution of the dye was
689 nm.

25 Other dyes used in this invention may also be
readily synthesized in accordance with the above process.

The sensitizing dye can be added to the silver
halide emulsion at any time before coating. The addition

1 amount of the dye may be varied in a wide range, but good
results can be obtained when it is added in an amount of
1 x 10⁻⁵ - 1 x 10⁻² mole for 1 mole of silver halide, the
optimum amount being dependent upon the type of silver
5 halide such as halogen composition, average grain size,
crystal habit, etc.

The silver halide emulsion used in the litho-
graphic printing plate of this invention may be silver
chloride, silver bromide, silver chlorobromide, silver
10 chloriodide, silver chlorobromiodide, etc. and preferably
a silver halide comprising at least 50 mole % of silver
chloride. The average grain size of these silver halides
is preferably in the range of 0.2 - 0.8 μ , though other
grain size are usable. The emulsion is preferably
15 monodispersed emulsion, 90% or more of total grains having
a size within $\pm 30\%$ of the average size. The grains are
preferably in the form of substantially cube or fourteen-
faced polyhedron, though those having other crystal habits
are not objectionable.

20 The binder used in the silver halide emulsion of
the lithographic printing plate of this invention is usually
gelatin which can be partially replaced with one or more
hydrophilic polymer binders such as starch, albumin,
sodium alginate, hydroxyethylcellulose, gum arabic, poly-
25 vinyl alcohol, carboxymethylcellulose, polyvinyl pyrrolidone,
polyacrylamide, styrene-maleic anhydride copolymer, poly-
vinyl methyl ether-maleic anhydride copolymer, etc. It is
further possible to use an aqueous dispersion (latex) of

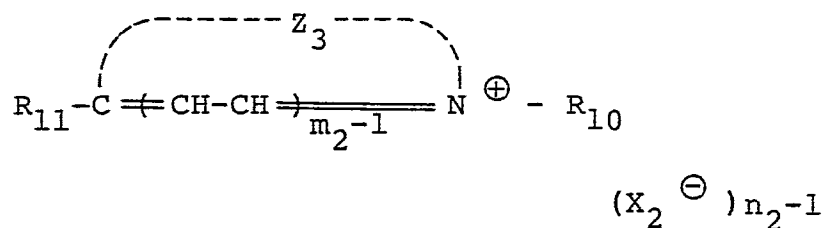
1 vinyl polymers.

The silver halide emulsion can be sensitized in various ways during its preparation or coating. The emulsion is preferably sensitized chemically by the methods
5 well known to the art by using, for example, sodium thio-sulfate, alkylthioureas, or gold compounds such as gold rhodanide and gold chloride or mixtures thereof.

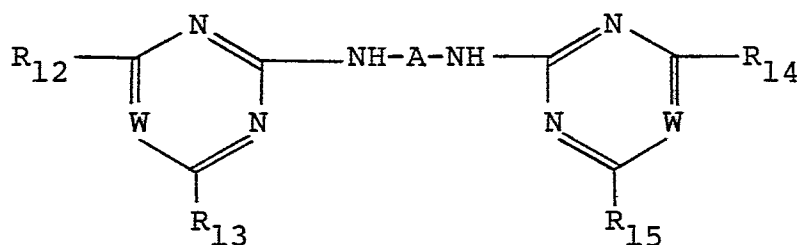
Those characteristics such as high sensitivity, high sharpness and high resolving power which are desirable
10 for the direct processing printing plates may be imparted by adding, at any time during the emulsion preparation, compounds of metals of Group VIII of the periodic table, such as, for example, salts of cobalt, nickel, rhodium, palladium, iridium and platinum. The amount of addition is
15 in the range of 10^{-8} - 10^{-3} mole for 1 mole of silver halide. The silver halide emulsion layer may contain other additives such as coating aids, hardeners, anti-foggants, matting agents (water-holding agents), and developing agents which are customarily used.

20 Higher sensitivity and printing endurance can be obtained by using the compounds represented by the following general formulas (A) and/or (B) in combination with the above mentioned near infrared sensitizing dyes in silver halide emulsion layer used in this invention.

General formula (A)



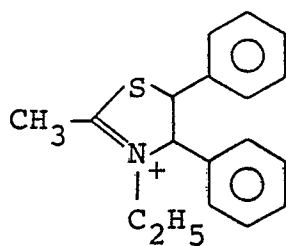
General formula (B)



- 1 In the general formula (A), Z_3 represents a group of atoms necessary for forming the 5- or 6-membered nitrogen containing heterocyclic ring as mentioned for Z_1 and Z_2 of the general formula (I); R_{11} represents hydrogen
- 5 atom or alkyl or aryl group as mentioned in the general formula (I); R_{10} represents an alkyl or alkenyl group as mentioned in the general formula (I); X_2^- represents an acid anion as mentioned for X of the general formula (I) with a proviso that if the compound has a betaine analogous
- 10 structure, X_2^- is not present; and m_2 and n_2 represent integers of 1 or 2.

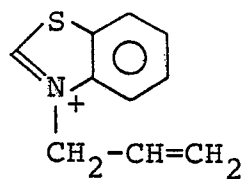
Typical examples of the compounds represented by the general formula (A) are shown below.

[A-1]



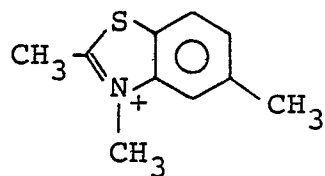
I⁻

[A-2]



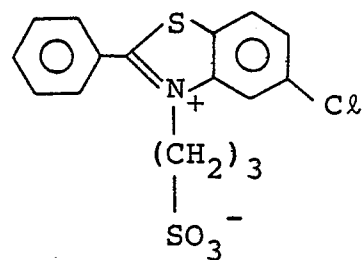
Br⁻

[A-3]

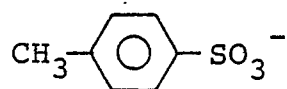
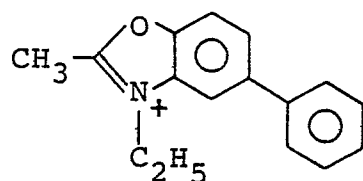


Cl⁻

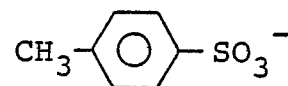
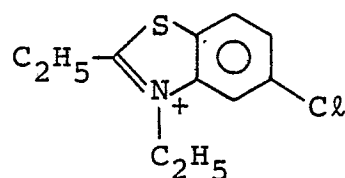
[A-4]



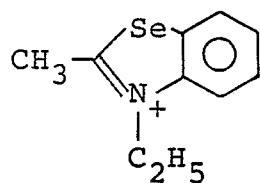
[A-5]



[A-6]

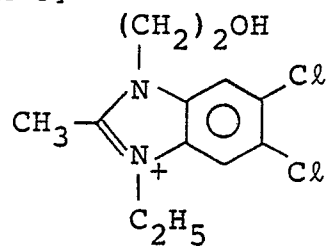


[A-7]



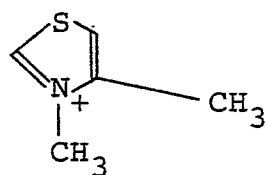
I⁻

[A-8]



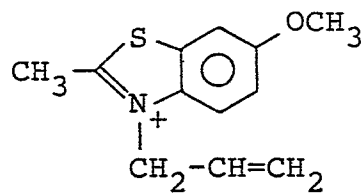
I⁻

[A-9]



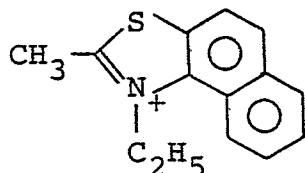
Br⁻

[A-10]



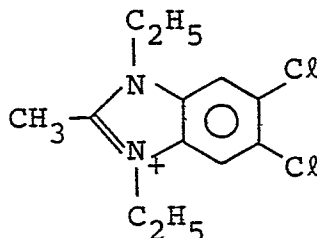
Br⁻

[A-11]



Br⁻

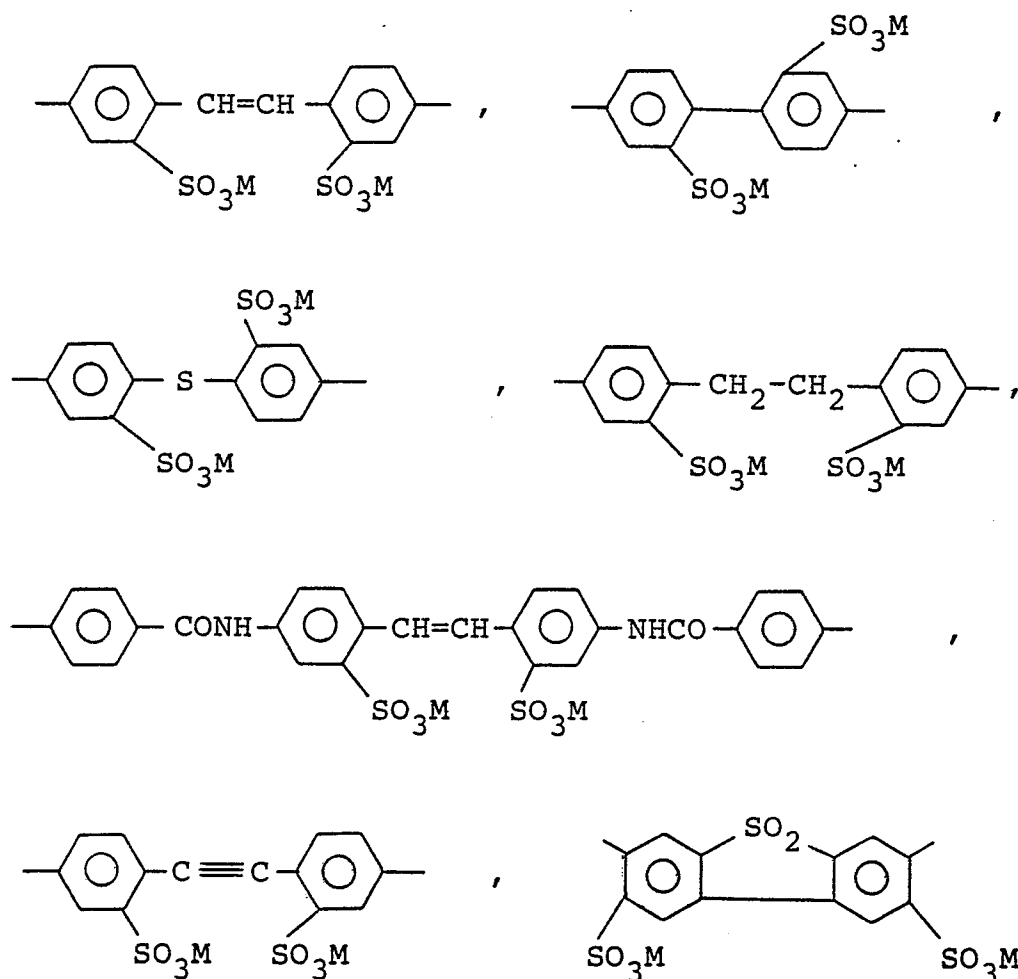
[A-12]

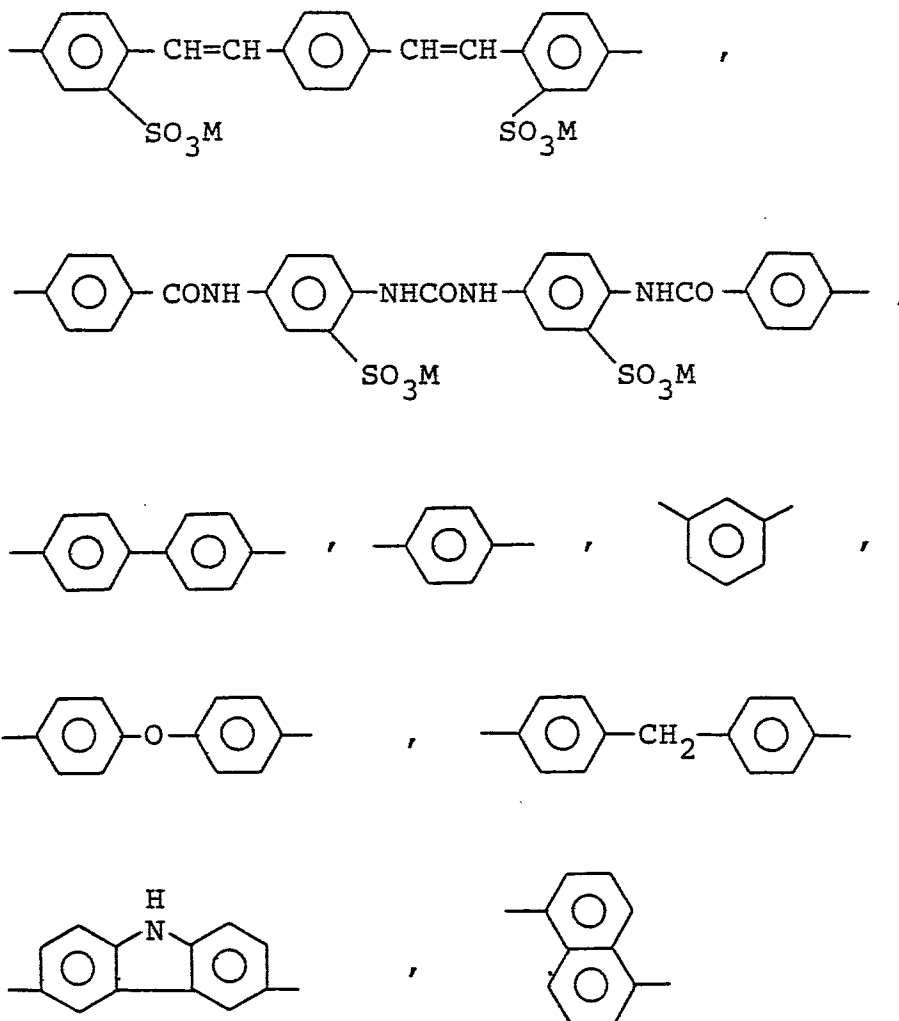


Br⁻

- 1 In the general formula (B), A represents a
- divalent aromatic residue which may contain-SO₃M group (M
- represents hydrogen atom or a cation such as sodium,
- potassium, etc.) with a proviso that when R₁₂- R₁₅ do not
- 5 contain -SO₃M group, A contains -SO₃M group; R₁₂ - R₁₅
- represent hydrogen atom, hydroxy group, aryloxy group (e.g.,
- phenoxy, naphthoxy, o-toloxo, p-sulfophenoxy, etc.),
- heterocyclic ring (e.g., morpholinyl, piperidyl, etc.),
- alkylthio group (e.g., methylthio, ethylthio, etc.), hetero-
- 10 cyclicthio group (e.g., benzothiazolylthio, benzoimidazolyl-
- thio, etc.), arylthio group (e.g., phenylthio, tolylthio,
- etc.), amino group, alkylamino group (e.g., methylamino,
- ethylamino, diethylamino, β-hydroxyethylamino, β-sulfo-

1 ethylamino, etc.), arylamino group (e.g., anilino, o-, m-
 or p-sulfoanilino, o-, m- or p-toluidino, o-, m- or p-
 carboxyanilino, o-, m- or p-chloroanilino, o-, m- or p-
 anisidino, o-acetaminoanilino, hydroxyanilino, naphthyl-
 5 amino, sulfonaphthylamino, etc.), heterocyclicamino group
 (e.g., 2-benzothiazolylamino, 2-piridylamino, etc.),
 aralkylamino group (e.g., benzylamino, o-, m- or p-anisyl-
 amino, etc.), mercapto group, or halogen atom, alkyl group
 or alkoxy group as mentioned for R_4 - R_9 of the general
 10 formula (I); W represents $-CH=$ or $-N=$, preferably $-CH=$,
 and examples of A are as follows:





1 Typical examples of the compounds represented by the general formula (B) are shown below.

(B-1) Disodium 4,4'-bis[4,6-di(benzothiazolyl-2-thio)pyrimidine-2-ylamino]stilbene-2,2'-disulfonate

5 (B-2) Disodium 4,4'-bis[4,6-di(benzothiazolyl-2-amino)pyrimidine-2-ylamino]stilbene-2,2'-disulfonate

(B-3) Disodium 4,4'-bis[4,6-di(naphthyl-2-oxy)pyrimidine-2-ylamino]stilbene-2,2'-disulfonate

(B-4) Disodium 4,4'-bis[4,6-di(naphthyl-2-oxy)pyrimidine-2-ylamino]dibenzyl-2,2'-disulfonate

10

- 1 (B-5) Disodium 4,4'-bis(4,6-dianilinopyrimidine-2-ylamino)stilbene-2,2'-disulfonate
- (B-6) Disodium 4,4'-bis[4-chloro-6-(2-naphthyloxy)pyrimidine-2-ylamino]biphenyl-2,2'-disulfonate
- 5 (B-7) Disodium 4,4'-bis[4,6-di(1-phenyltetrazolyl-5-thio)pyrimidine-2-ylamino]stilbene-2,2'-disulfonate
- (B-8) Disodium 4,4'-bis[4,6-di(benzoimidazolyl-2-thio)pyrimidine-2-ylamino]stilbene-2,2'-disulfonate
- (B-9) Disodium 4,4'-bis(4,6-diphenoxypyrimidine-2-ylamino)stilbene-2,2'-disulfonate
- 10 (B-10) Disodium 4,4'-bis(4,6-diphenylthiopyrimidine-2-ylamino)stilbene-2,2'-disulfonate
- (B-11) Disodium 4,4'-bis(4,6-dimercaptopyrimidine-2-ylamino)biphenyl-2,2'-disulfonate
- 15 (B-12) Disodium 4,4'-bis(4,6-dianilino-triazine-2-ylamino)stilbene-2,2'-disulfonate
- (B-13) Disodium 4,4'-bis(4-anilino-6-hydroxy-triazine-2-ylamino)stilbene-2,2'-disulfonate
- (B-14) Disodium 4,4'-bis(4-naphthylamino-6-anilino-
- 20 triazine-2-ylamino)stilbene-2,2'-disulfonate

Either one of the compound represented by the general formula (A) or the compound represented by the general formula (B) may be added, but two or more of the compounds represented by the general formula (A) or two
25 or more of the compounds represented by the general formula (B) may be added or at least one of the compound represented by the general formula (A) and at least one of the compound

1 represented by the general formula (B) may be added in
combination.

Which compound is more effective for the sensi-
tizing dye represented by the general formulas (I) - (V),
5 the compound represented by the general formula (A) or (B),
depends on the kinds of the sensitizing dyes and the
compounds and combination thereof. In general, addition
of the compound represented by the general formula (A) and
the compound represented by the general formula (B) in
10 combination is more advantageous.

Addition amount of the compounds represented by
the general formulas (A) and (B) is 1×10^{-4} - 3×10^{-1}
mole, preferably 5×10^{-4} - 2×10^{-1} mole per 1 mole of
silver halide, respectively.

15 A subbing layer for improving adhesion or an
undercoat layer which may contain a coloring agent such as
carbon black and a compound absorbing a light of at least
700 mμ may be provided below the silver halide emulsion
layer (and above the support). This undercoat layer may
20 further contain a developing agent or a matting agent.

An image receiving layer is provided above the
silver halide emulsion layer, namely, as an outermost
surface layer. The image receiving layer contains known
physical development nuclei such as metals including
25 antimony, bismuth, cadmium, cobalt, palladium, nickel,
silver, lead, zinc, etc. and sulfides thereof, etc. The
image receiving layer may contain at least one hydrophilic
colloid such as gelatin, carboxymethylcellulose, gum

1 arabic, sodium alginate, hydroxyethyl starch, dialdehyde
starch, dextrin, hydroxyethylcellulose, polystyrenesulfonic
acid, a vinylimidazole-acrylamide copolymer, polyvinyl
alcohol, etc. This hydrophilic colloid contained in the
5 image receiving layer is preferably 0.1 g/m^2 or less.
The image receiving layer may further contain hygroscopic
substances or wetting agents such as sorbitol, glycerol,
etc. It may further contain anti-scumming pigments such
as barium sulfate, titanium dioxide, China clay, silver,
10 etc., developing agents such as hydroquinone and hardeners
such as formaldehyde, dichloro-S-triazine, etc.

The supports may be paper, films such as cellulose
acetate film, polyvinyl acetal film, polystyrene film,
polypropylene film, polyethylene terephthalate film, etc.,
15 composite films such as polyester, polypropylene, or
polystyrene films coated with polyethylene film; metals;
metallized paper; or metal/paper laminates. A paper
support coated on one or both sides with an olefin polymer
such as polyethylene is also useful. These supports may
20 contain compounds having antihalation power.

The processing solution for development used in
this invention may contain alkaline substances such as
sodium hydroxide, potassium hydroxide, lithium hydroxide,
sodium tertiary phosphate, etc.; preservatives such as
25 sulfites, etc.; silver halide solvents such as thiosulfates,
cyclic imides, thiosalicylic acid, amines, etc.; thickening
agents such as hydroxyethylcellulose, carboxymethylcellulose,
etc.; antifoggants such as potassium bromide, l-phenyl-

1 5-mercaptotetrazole, compounds described in Japanese Patent
Unexamined Publication (Kokai) No. 26201/72, etc.; develop-
ing agents such as hydroquinone, 1-phenyl-3-pyrazolidone,
etc.; development modifiers such as polyoxyalkylene
5 compounds, onium compounds, etc.

When the silver complex diffusion transfer
process is carried out, the developing agent may be
contained in the silver halide emulsion layer and/or the
image receiving layer or other water permeable layers
10 contiguous to the image receiving layer as described in
British Patent Nos. 1,000,115, 1,012,476, 1,017,273, and
1,042,477. Therefore, in such case, use may be made of a
so-called "alkaline activating solution" containing no
developing agent.

15 The lithographic printing plates made in accord-
ance with this invention can be rendered ink receptive or
enhanced in ink receptivity by use of such compounds as
described in Japanese Patent Examined Publication (Kokoku)
No. 29723/73 and U.S. Patent No. 3,721,539.

20 The printing method, etch solution and damping
solution are those which are known to the art.

The following nonlimiting examples further
illustrate this invention.

Example 1

25 On one side of a subbed polyester film support,
was provided a matting layer containing powdered silica
of 5 μ in average particle size. On another side, was

1 provided an undercoat layer (adjusted to pH 4) containing
carbon black and 20% by weight based on the photographic
gelatin of powdered silica, 7 μ in average particle size.
On this undercoat layer was provided a high speed silver
5 chloriodobromide emulsion layer (Br: 3 mol %, I: 0.4 mole %
and Cl: 96.6 mole % and adjusted to pH 4.0) containing 5%
by weight (based on photographic gelatin) of powdered
silica, 7 μ in average particle size, which had been
chemically sensitized with a gold compound and then
10 spectrally sensitized.

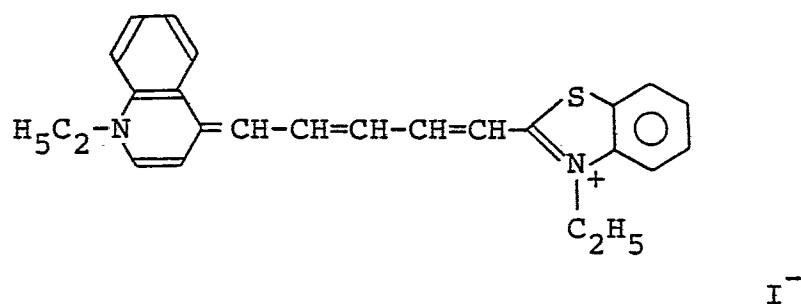
The application rate of gelatin in the undercoat
layer was 3.0 g/m², that of gelatin in the emulsion layer
was 1.0 g/m² and that of silver halide in terms of silver
nitrate was 1.0 g/m². These undercoat layer and emulsion
15 layer contained 5.0 mg of formaldehyde as a hardener for
1 g of gelatin. After drying, the coated support was
heated at 40°C for 14 days. Then, the emulsion layer was
overcoated with a nuclei coating composition described in
Japanese Patent Unexamined Publication (Kokai) No. 21602/78
20 (the polymer used was No. 3 acrylamide-imidazole copolymer
and hydroquinone was contained in an amount of 0.8 g/m²)
and was dried to obtain a light sensitive material for
lithographic printing plate. The above mentioned silver
halide emulsion contained 5×10^{-6} mole of rhodium
25 chloride for 1 mole of silver halide which had been
added during physical ripening of the emulsion. The silver
halide grains were in substantially cubic form and were
0.3 μ in average grain size and 90% or more of the total

1 grains were distributed within $\pm 30\%$ of the average grain size.

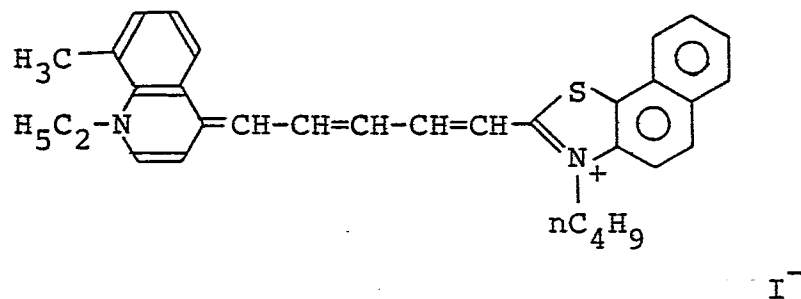
Eleven light sensitive materials for lithographic printing plates were prepared in the same manner as above except that 10^{-3} mole (for 1 mole of silver halide) of each sensitizing dye shown in Table 1 was added to each silver halide emulsion.

The following dyes were used as comparative dyes.

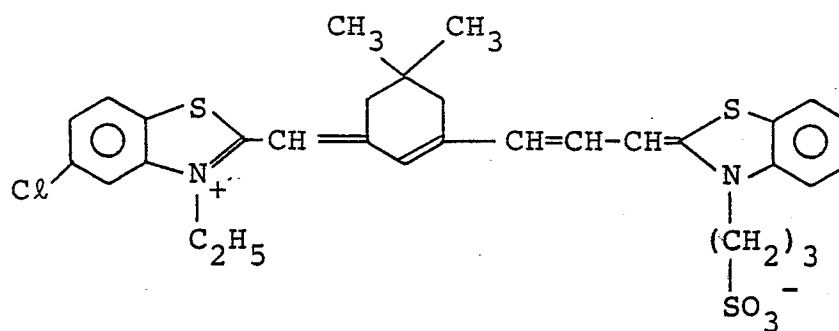
[A]



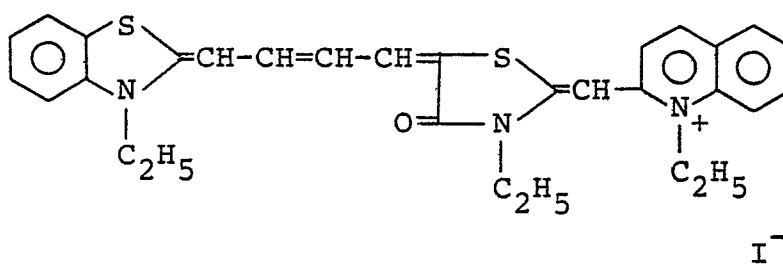
[B]



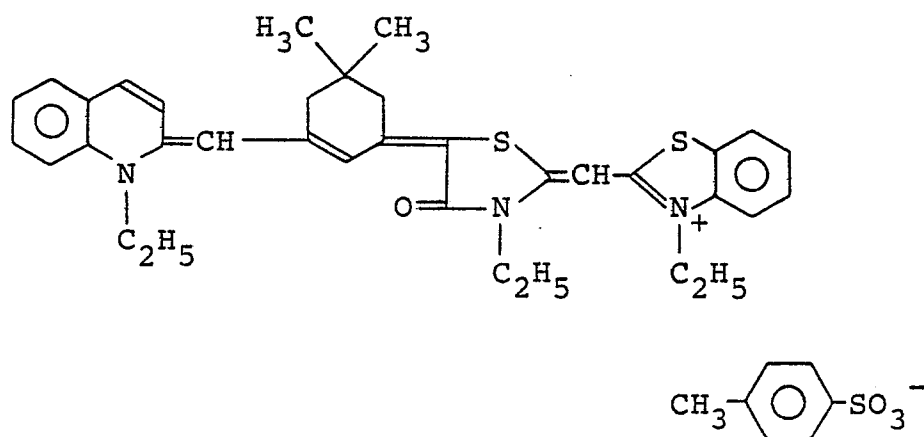
[C]



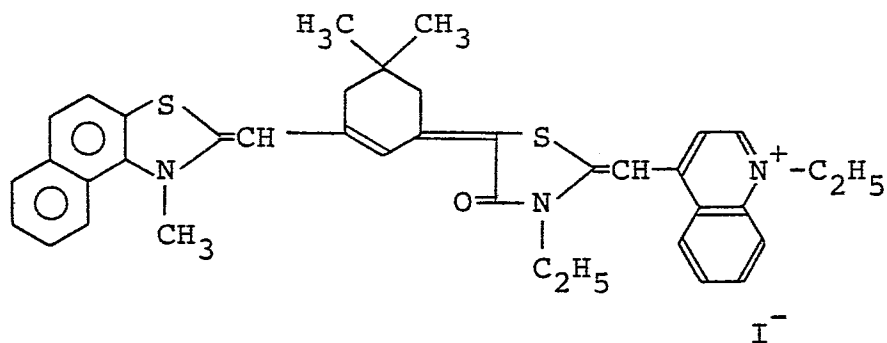
[D]



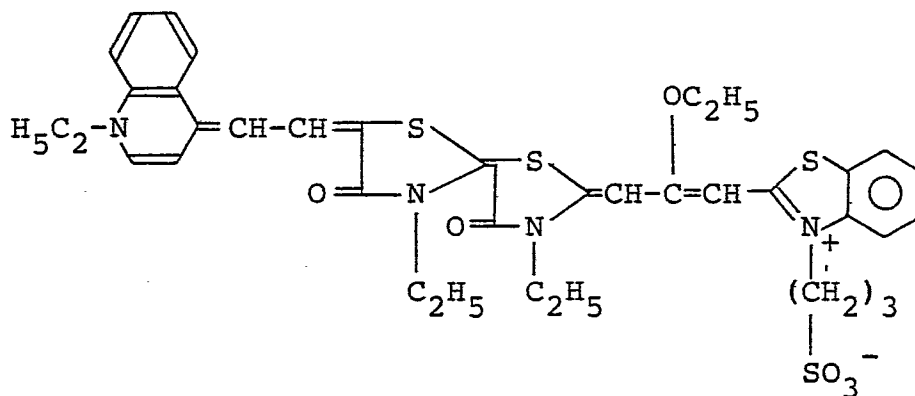
[E]



[F]



[G]



1 Each of these light sensitive materials in close
 contact with an original of a film block copy containing
 thin line images was exposed to a light source to which
 was attached a dark red filter SC-70 (manufactured by Fuji
 5 Photo Film Co., Ltd.) which transmitted light having wave-
 lengths longer than about 700 mμ. The exposure was carried
 out by subjecting the material to a flash exposure for a
 period in the range of 10⁻⁴ - 10⁻⁵ seconds depending on
 sensitivity difference so that nearly the same print
 10 exposures were attained. These were used as samples for

1 printing test.

Separately the light sensitive materials were subjected to a flash exposure for 10^{-5} seconds through an optical wedge to a light source to which the dark red
5 filter SC-70 was attached. These were used as samples for sensitometry.

After the exposure, the light sensitive materials were developed with the following diffusion transfer developer.

10	<u>Developer</u>	
	Water	700 ml
	Sodium hydroxide	18 g
	Potassium hydroxide	7 g
	Anhydrous sodium sulfate	50 g
15	2-Mercaptobenzoic acid	1.5 g
	2-Methylamino ethanol	15 g
	Water to make up 1 l	

After the development treatment, these materials were passed between two squeeze rollers to remove excess
20 developer, immediately thereafter treated with the following neutralizing solution at 25°C for 20 seconds, passed between squeeze rollers to remove excess solution and dried at room temperature.

	<u>Neutralizing solution</u>	
	Water	600 ml
25	Citric acid	10 g

1	Sodium citrate	35 g
	Colloidal silica (20% solution)	5 ml
	Ethylene glycol	5 ml
	Water was added to make up 1 l.	

5 Sensitivity of this light sensitive materials
and printing endurance of the resulting lithographic
printing plates are shown in Table 1. The sensitivity was
evaluated by the exposure required before the precipita-
tion of the transferred silver had no more been observed
10 and expressed as a relative value by assuming the sensitivity
in the case of the sensitizing dye (I-5) to be 1.0 as
standard. The printing endurance was evaluated in terms
of the number of copies delivered before the printing had
become impossible owing to the occurrence of scumming or
15 partial disappearance of silver image and expressed in
grade number rated in accordance with the following
criteria.

Grade No.	Number of copies
1	<4000
2	4000 - 6000
3	6000 - 8000
4	8000 - 10000
5	>10000

The printing for the above tests was carried out
by mounting a sheet to which each of the samples was
20 applied, on an offset printing machine, applying the

- 1 following etch solution to allover the plate surface and using the following damping solution. The printing machine was A.B. Dick 350 CD (Trademark for offset printing machine supplied by A.B. Dick Co.).

Etch solution

Water	600 ml
Isopropyl alcohol	400 ml
Ethylene glycol	50 ml
3-mercapto-4-acetamido- 5-n-heptyl-1,2,4-triazole	1 g

Damping solution

o-Phosphoric acid	10 g
Nickel nitrate	5 g
Sodium sulfate	5 g
Ethylene glycol	100 g
Colloidal silica (20% solution)	28 g
Water was added to make up 2 l.	

Table 1

Sensitizing dyes	Relative sensitivity	Printing endurance
(I - 1)	1.2	4
(I - 5)	1.0	4
(I - 10)	1.3	3
(I - 16)	1.2	4
A	0.4	2
B	0.5	2
C	0.2	1
D	0.1	3
E	0.2	2
F	0.6	1
G	0.2	4

1 Example 2

Light sensitive materials were prepared in the same manner as in Example 1 except that a silver chloro-iodide containing 0.2 mole % of silver iodide was used as the silver halide emulsion and dyes shown in Table 2 were used as the sensitizing dyes. Then, in the same manner as in Example 1, lithographic printing plates were made therefrom and printing was carried out to obtain the results as shown in Table 2. The sensitivity was expressed as a relative value by assuming the sensitivity in the case of sensitizing dye (I-3) to be 1.0 as standard.

Table 2

Sensitizing dyes	Relative sensitivity	Printing endurance
(I - 3)	1.0	4
(I - 7)	0.9	5
(I - 8)	0.9	5
(I - 12)	0.7	5
(I - 18)	1.1	4

1 Example 3

Each of the samples obtained in Examples 1 and 2 was kept at 50°C and 80% RH for 3 days and subjected to the same tests as those of Example 1. The comparative
5 samples had substantially no sensitivity to the radiation of about 780 mμ due to further conspicuous desensitization while the samples of this invention underwent at most about 10% of desensitization and were satisfactorily high in shelf stability.

10 Example 4

Twelve light sensitive materials and lithographic printing plates were prepared in the same manner as in Example 1 except that the dyes shown in Table 3 were used in an amount of 5×10^{-4} mole for 1 mole of silver halide
15 as sensitizing dyes used in the silver halide emulsion and they were subjected to the same tests as in Example 1 except that dye (II-7) was employed as standard for

1 evaluation of sensitivity. The results are shown in Table 3.

Table 3

Sensitizing dyes	Relative sensitivity	Printing endurance
(II - 2)	0.8	4
(II - 3)	0.9	4
(II - 4)	0.9	4
(II - 5)	0.8	4
(II - 7)	1.0	4
A	0.6	2
B	0.7	2
C	0.3	1
D	0.2	3
E	0.3	2
F	0.9	1
G	0.3	4

Example 5

Light sensitive materials were prepared in the same manner as in Example 1 except that a silver chloride emulsion containing 0.2 mole % of silver iodide was used as the silver halide emulsion and that dyes as shown in the following Table 4 were used as the sensitizing dyes. Then, in the same manner as in Example 1, lithographic printing plates were made therefrom. These samples were subjected to the same tests as in Example 1 except that

1 the sensitivity was evaluated using the sensitizing dye
(II-1) as standard. The results are shown in Table 4.

Table 4

Sensitizing dyes	Relative sensitivity	Printing endurance
(II - 1)	1.0	4
(II - 10)	1.2	5
(II - 11)	0.9	5

Example 6

The samples obtained in Examples 4 and 5 were
5 kept at 50°C and 80% RH for 3 days and thereafter were
subjected to the same tests as in Example 1 to find that
the comparative samples had substantially no sensitivity
to the light of about 780 mμ owing to further conspicuous
desensitization while the samples of this invention
10 underwent desensitization of at most about 10% and were
sufficiently high in shelf stability.

Example 7

Example 1 was repeated except that dyes shown in
the following Table 5 were used as the sensitizing dyes.
15 The following dye (H) was also used as a comparative dye.

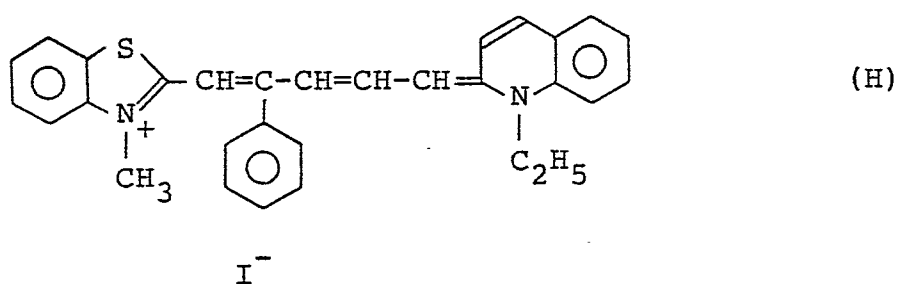


Table 5

Sensitizing dyes	Relative sensitivity	Printing endurance
[III - 3]	1.0	3
[III - 5]	1.2	4
[III - 9]	1.1	4
[III - 10]	1.1	4
A	0.7	2
B	0.8	2
C	0.3	1
D	0.2	3
E	0.3	2
F	1.0	1
G	0.3	4
H	0.9	1

1 Example 8

Light sensitive materials were prepared in the same manner as in Example 1 except that a silver chloriodide emulsion containing 0.2 mole % of silver iodide was used

1 as the silver halide emulsion and the sensitizing dyes
shown in the following Table 6 were used. In the same
manner as in Example 1, lithographic printing plates
were made therefrom. These samples were subjected to the
5 same tests as in Example 1 with using the sensitizing dye
(III-2) as standard for evaluation of sensitivity. The
results are shown in Table 6:

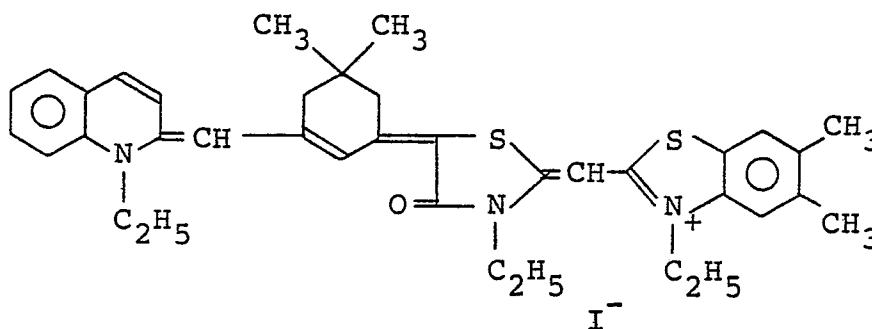
Table 6

Sensitizing dyes	Relative sensitivity	Printing endurance
[III - 2]	1.0	5
[III - 9]	1.2	4
[III - 11]	1.1	4

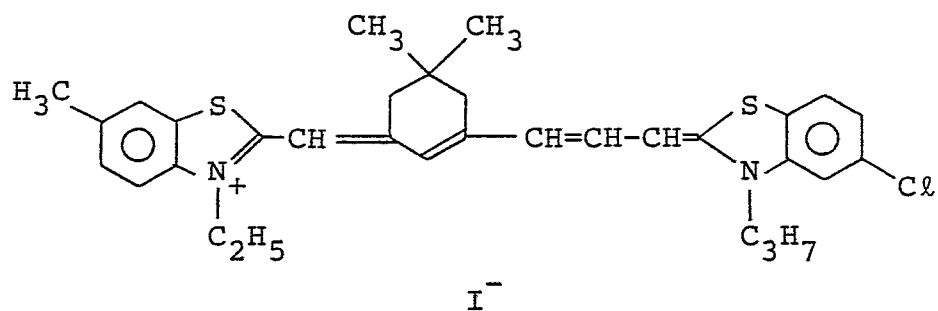
Example 9

Example 1 was repeated except that dyes shown in
10 Table 7 were used as sensitizing dyes. The following
dyes (I), (J) and (K) were also used as comparative dyes.

[I]



[J]



[K]

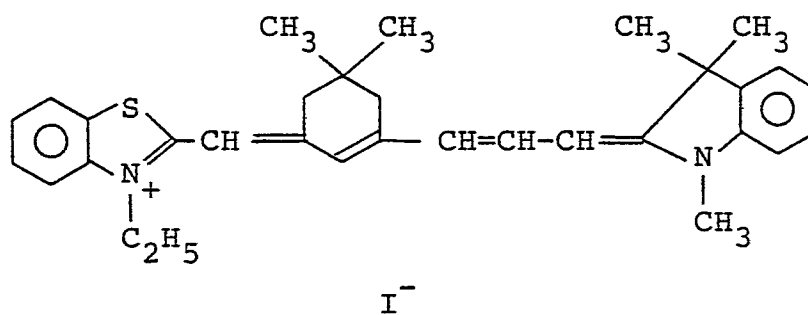


Table 7

Sensitizing dyes	Relative sensitivity	Printing endurance
[IV - 1]	1.0	4
[IV - 4]	1.0	4
[IV - 7]	1.3	4
A	0.8	2
B	0.9	2
C	0.4	1
D	0.3	3
E	0.4	2
F	1.2	1

- cont'd -

Table 7 (cont'd)

G	0.4	4
H	1.0	1
I	1.1	1
J	0.8	2
K	0.2	4

1 Example 10

Light sensitive materials and lithographic printing plates were prepared in the same manner as in Example 1 except that a silver chloriodide emulsion containing 0.2 mole % of silver iodide was used as silver halide emulsion and sensitizing dyes shown in the following Table 8 were used. These samples were subjected to the same tests as in Example 1 with using the sensitizing dye (IV-1) as standard for evaluation of sensitivity. The results are shown in Table 8.

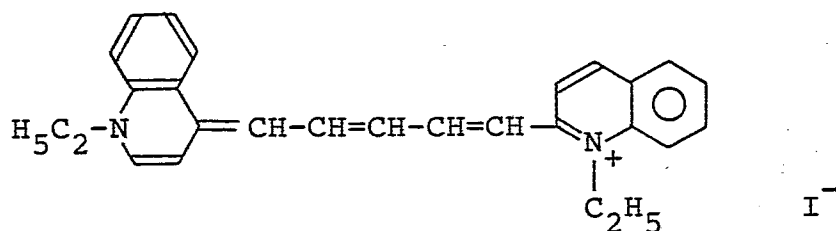
Table 8

Sensitizing dyes	Relative sensitivity	Printing endurance
[IV - 1]	1.0	4
[IV - 2]	1.2	4
[IV - 9]	1.2	4

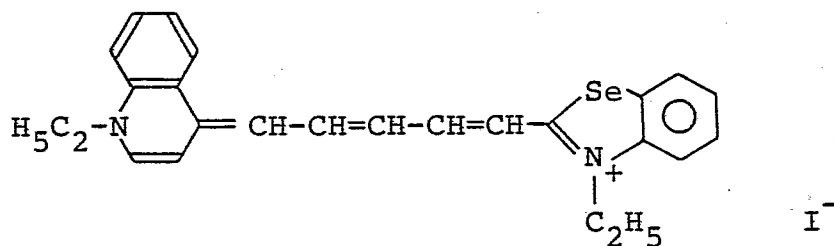
1 Example 11

Example 1 was repeated except that dyes shown in the following Table 9 were used as sensitizing dyes. The following dyes (L), (M) and (N) were also used as comparative dyes.

[L]



[M]



[N]

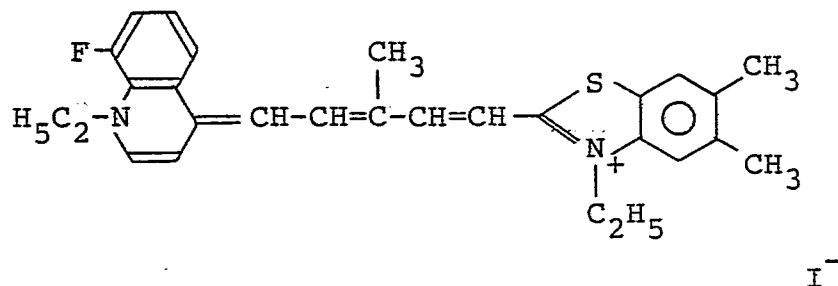


Table 9

Sensitizing dyes	Relative sensitivity	Printing endurance
[V - 1]	1.0	4
[V - 2]	1.2	4
[V - 4]	1.3	4
[V - 6]	1.3	4
[V - 10]	1.2	4
A	0.7	2
B	0.7	2
C	0.4	2
D	0.2	3
E	0.4	2
F	1.1	2
G	0.3	4
J	0.8	2
L	0.6	2
M	0.5	3
N	0.3	3

1 Example 12

Light sensitive materials and lithographic printing plates were prepared in the same manner as in Example 1 except that a silver chloriodide emulsion containing 0.3 mole % of silver iodide was used and the sensitizing dyes shown in the following Table 10 were used. The samples were subjected to the same tests as in Example

- 1 1 with using the sensitizing dye (V-1) as standard for evaluation of sensitivity.

Table 10

Sensitizing dyes	Relative sensitivity	Printing endurance
[V - 1]	1.0	4
[V - 5]	0.9	4
[V - 8]	1.2	4
[V - 12]	1.0	4

Example 13

On one side of a subbed polyester film support, was provided a matting layer containing powdered silica of 5 μ in average particle size. On another side, was provided an undercoat layer (adjusted to pH 4.5) containing carbon black and 20% by weight (based on photographic gelatin) of powdered silica of 7 μ in average particle size. On the undercoat layer was provided a silver halide emulsion layer (adjusted to pH 4.5) containing 5% by weight (based on photographic gelatin) of powdered silica of 7 μ in average particle size which had been chemically sensitized with a gold compound and thiosulfate.

The silver halide emulsion comprised silver chloride crystals of substantially cubic form and contained 5 x 10⁻⁶ mole of rhodium chloride for 1 mole of silver

1 halide. The silver halide grains were 0.4μ in average grain size and 90% or more of the total grains were distributed within $\pm 30\%$ of the average grain size.

The application rate of gelatin in the under-
5 coat layer was 3.0 g/m^2 , that of gelatin in the emulsion layer was 1.0 g/m^2 and that of the silver halide was 1.2 g/m^2 in terms of silver nitrate. Both the undercoat layer and the emulsion layer contained 5.0 mg of formaldehyde as hardener for 1 g of gelatin. After drying, the coated
10 support was heated at 40°C for 14 days. The emulsion layer was then coated with a nuclei coating composition of plate No. 11 in Example 1 of Japanese Patent Unexamined Publication (Kokai) No. 103104/79.

Light sensitive materials for lithographic
15 printing plate (samples A-H) were prepared by the same procedure as mentioned above except that sensitizing dyes of the general formula (II) and the compounds of the general formulas (A) and (B) were added to the emulsion layer as shown in Table 11.

20 These samples immediately after the preparation (kept for a whole day and night at 35°C) and after kept at 50°C and 80% RH for 4 days were exposed in the following manner.

Each of the samples in close contact with an
25 original of film block copy containing thin line images was subjected to a flash exposure to a light source having a dark red filter SC-70 (manufactured by Fuji Photo Film Co.) which transmitted the light having a wavelength

1 longer than about 700 nm for a period in the range of
 10^{-3} - 10^{-5} seconds depending on the difference in sensi-
 tivity so that substantially the same print exposure was
 obtained. These were used as samples for printing tests.

5 Separately, each of the samples was subjected to
 a flash exposure to a light source having the dark red
 filter SC-70 through an optical wedge for 10^{-5} seconds.
 These were used as samples for sensitometry.

Each of the imagewise exposed samples was
 10 developed with the following diffusion transfer developer
 at 25°C for 30 seconds.

After development, the sample was passed between
 two squeeze rollers to remove excess developer, immediately
 thereafter treated with the neutralizing solution used in
 15 Example 1 at 25°C for 20 seconds, passed between squeeze
 rollers to remove excess solution and then dried at room
 temperature.

Diffusion transfer developer

Water	700 ml
Sodium hydroxide	18 g
Potassium hydroxide	7 g
Anhydrous sodium sulfate	50 g
Hydroquinone	13 g
Phenidone	1.5 g
2-Mercaptobenzoic acid	2 g
Uracil	2 g
2-Methylamino ethanol	30 ml

5-Phenyl-2-mercapto-1,3,4-
oxadiazole

0.1 g

Water was added to make up 1 l.

- 1 Printing endurance was evaluated in the same way as in Example 1 except that it was expressed in grade number rated in accordance with the following criteria.

Grade No.	Number of copies
1	<1000
2	1000 - 3000
3	3000 - 5000
4	5000 - 7000
5	>7000

- 5 The sensitivity was evaluated by the exposure required before the precipitation of the transferred silver had no more been observed and expressed as a relative value by assuming the sensitivity of Samples A and E (containing only dyes) just after preparation to be 100.

Table 11

Samples	Sensitizing dyes ($\times 10^{-4}$ mole)	Compounds of formula (A) (mg)	Compounds of formula (B) (mg)
A	(II-14) 5		
B	(II-14) 5	(A-2) 200	
C	(II-14) 5		(B-3) 200
D	(II-14) 5	(A-2) 200	(B-3) 200
E	(I-2) 5		
F	(I-2) 5	(A-6) 200	
G	(I-2) 5		(B-3) 200
H	(I-2) 5	(A-6) 200	(B-3) 200

The addition amount was per 1 mole of silver halide. This is the same in the following.

The results are shown in Table 12.

Table 12

Samples	Immediately after preparation		Kept at 50°C, 80% RH for 4 days	
	Sensitivity	Printing endurance	Sensitivity	Printing endurance
A	100 (standard)	4	60	2
B	110	4	90	4
C	140	4	120	4
D	170	4	150	4
E	100 (standard)	4	70	2
F	130	4	120	4
G	110	4	90	4
H	160	5	140	4

1 Example 14

Example 13 was repeated except that the dyes and the compounds were used as shown in Table 13. The results are shown in Table 14.

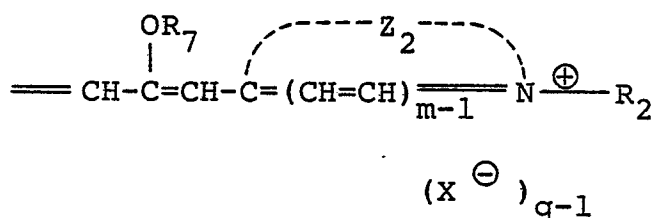
Table 13

Samples	Sensitizing dyes ($\times 10^{-4}$ mole)	Compounds of formula (A) (mg)	Compounds of formula (B) (mg)
A	(IV-4) 5		
B	(IV-4) 5	(A-2) 200	
C	(IV-4) 5		(B-3) 200
D	(IV-4) 5	(A-2) 200	(B-3) 200
E	(V-2) 5		
F	(V-2) 5	(A-6) 200	
G	(V-2) 5		(B-3) 200
H	(V-2) 5	(A-6) 200	(B-3) 200

Table 14

Samples	Immediately after preparation		Kept for 3 days	
	Sensitivity	Printing endurance	Sensitivity	Printing endurance
A	100 (standard)	3	70	2
B	190	4	200	4
C	220	4	240	4
D	360	4	390	4
E	100 (standard)	3	40	1
F	160	4	140	3
G	110	4	90	4
H	140	4	130	4

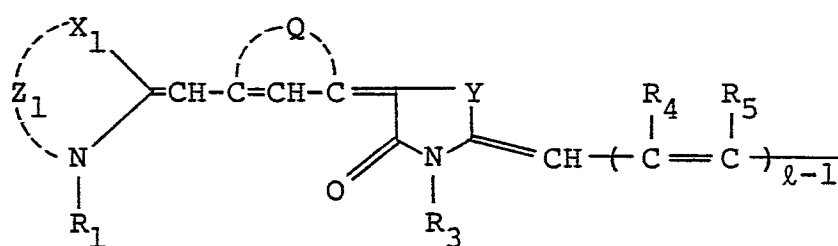
1. A light sensitive material for lithographic printing plate which comprises a support and at least a silver halide emulsion layer and a surface physical development nuclei layer provided on said support wherein said silver halide emulsion layer contains at least one of the sensitizing dyes represented by the following general formulas (I), (II), (III), (IV) and (V):

$$R_1-N-(CH=CH)_{n-1}-C \equiv C - C(R_4)=C(R_5)-C(R_6)-[CH_2-CH(Y)-N(R_3)-CO]_x \quad (I)$$


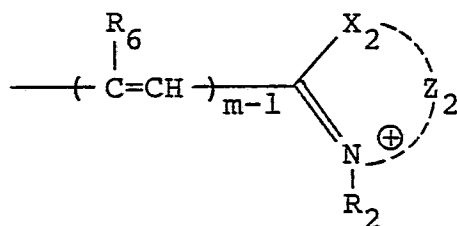
wherein Z_1 and Z_2 which may be identical or different represent a group of atoms which are necessary to form a 5- or 6-membered nitrogen containing heterocyclic ring; R_1 , R_2 and R_7 which may be identical or different represent alkyl group or alkenyl group; R_3 represents alkyl group, alkenyl group or aryl group; R_4 - R_6 which may be identical or different represent hydrogen atom, alkyl group or aryl

group; ℓ represents 0 or 1 with a proviso that when ℓ is 1, R_4 and R_5 may link with each other to form a 5- or 6-membered ring; Y represents sulfur atom, oxygen atom or $>N-R_8$ (R_8 represents alkyl group); X represents acid anion; and m, n and q represent 1 or 2.

General formula (II)



(II)



$(X^\ominus)_{q-1}$

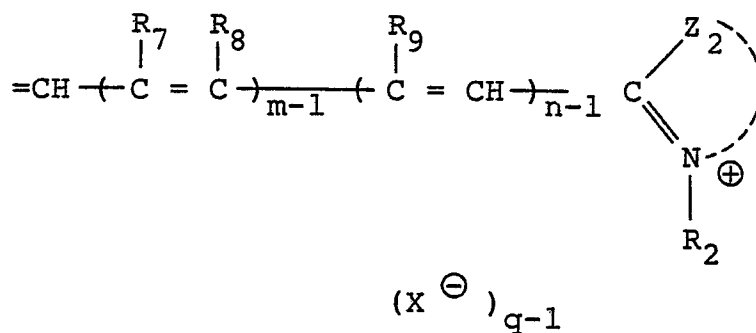
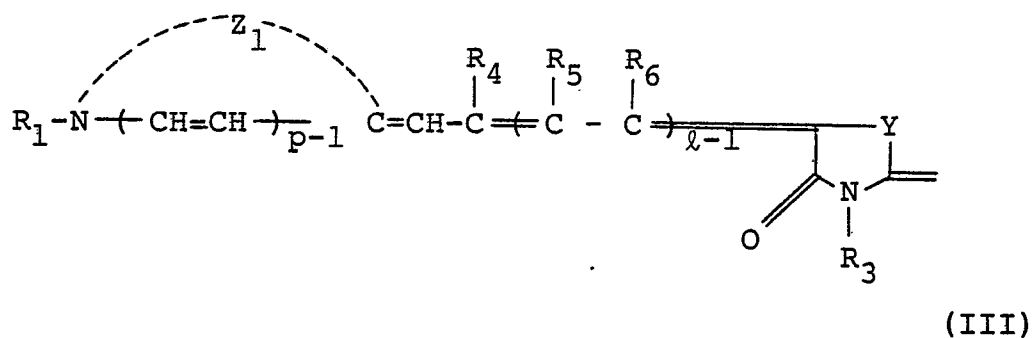
wherein X_1 and X_2 which may be identical or different represent oxygen atom, sulfur atom, selenium atom, $>N-R_7$

(R_7 represents an alkyl group) or $>C \begin{matrix} R_8 \\ R_9 \end{matrix}$ (R_8 and R_9

represent alkyl group); Z_1 and Z_2 which may be identical or different represent a group of atoms necessary for forming a 5-membered nitrogen containing heterocyclic ring; R_1 and R_2 which may be identical or different represent alkyl group, or alkenyl group; R_3 represents an alkyl group, an

alkenyl group or an aryl group; R_4 , R_5 and R_6 which may be identical or different represent hydrogen atom, halogen atom, alkyl group or aryl group; Y represents sulfur atom, oxygen atom or $>N-R_{10}$ (R_{10} represents an alkyl group); Q represents a group of atoms necessary for forming a 5- or 6-membered ring by linking with carbon atom of methine chain; X represents an acid anion; and l , m and q represent 1 or 2.

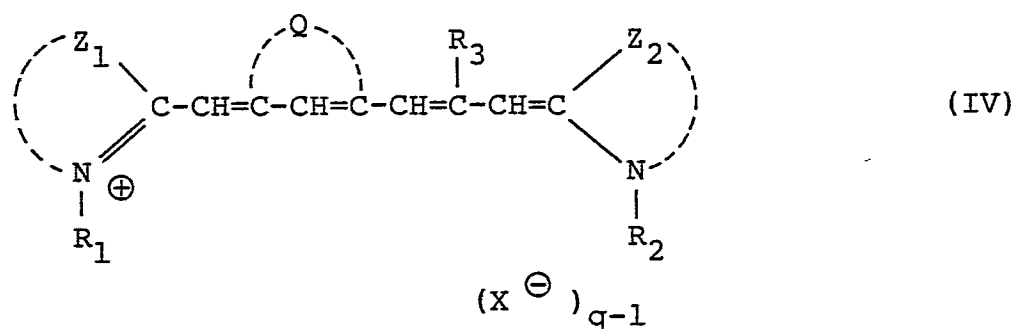
General formula (III)



wherein Z_1 represents a group of atoms necessary for forming a 5- or 6-membered nitrogen containing heterocyclic ring; Z_2 represents a group of atoms necessary for forming a 5-membered nitrogen containing heterocyclic ring; R_1 and R_2 which may be identical or different represent alkyl group

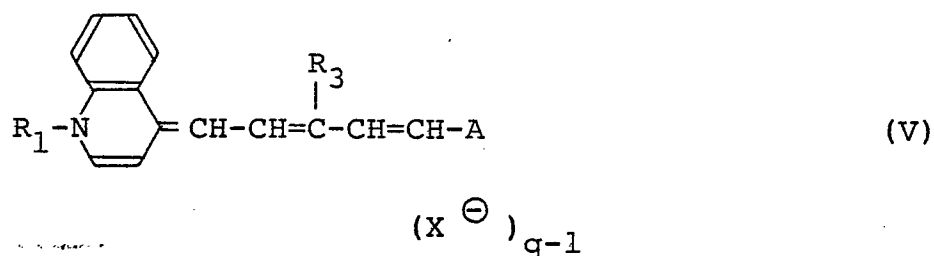
or alkenyl group; R_3 represents an alkyl group, an alkenyl group or an aryl group; $R_4 - R_9$ which may be identical or different represent hydrogen atom, halogen atom, alkyl group or aryl group; Y represents sulfur atom, oxygen atom $>N-R_{10}$ (R_{10} represents an alkyl group); X represents an acid anion; l, m, n, p and q represent 1 or 2 with a proviso that when m and n are both 1, l is 2.

General formula (IV)

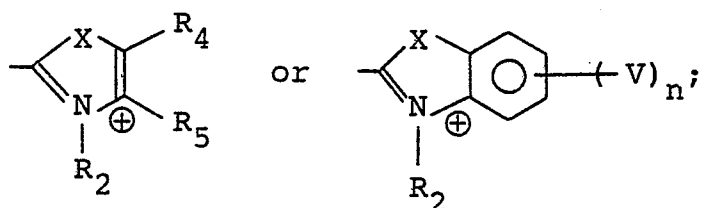


wherein Z_1 and Z_2 which are different represent thiazole ring, selenazole ring or oxazole ring which may have a condensed ring; R_1 and R_2 which may be identical or different represent alkyl group or alkenyl group; R_3 represents hydrogen atom, an alkyl group or an aryl group; Q represents a group of atoms necessary for forming a 5- or 6-membered ring by linking with carbon atom of methine chain; X represents an acid anion; and q represents 1 or 2.

General formula (V)



wherein A represents

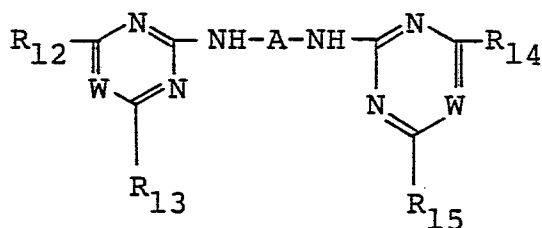


X represents sulfur atom, selenium atom, oxygen atom or N-R₆ (R₆ represents an alkyl group); R₄ and R₅ represent hydrogen atom, alkyl group or aryl group with a proviso that R₄ and R₅ cannot be both hydrogen atoms; V represents an alkyl group, an alkoxy group, an aryl group, an alkoxycarbonyl group, an alkenyl group, a carboxy group, hydroxy group or a halogen atom; n represents 0 or an integer of 1-4 and when n is 0, V forms naphthothiazole ring; R₁ and R₂ represent alkyl group or alkenyl group; R₃ represents hydrogen atom, an alkyl group or an aryl group; X represents an acid anion; and q represents 1 or 2.

2. A light sensitive material for lithographic printing plate according to claim 1 wherein the silver halide emulsion layer additionally contains at least one of the compounds represented by the following general formulas (A) and (B):

$$R_{11}-C \equiv \overbrace{CH-CH}^{Z_3} \equiv N^{\oplus}-R_{10} \quad (A)$$

General formula (B)



wherein A represents a divalent aromatic residue which may contain $-\text{SO}_3\text{M}$ (M represents hydrogen atom or a cation) with a proviso that when $\text{R}_{12} - \text{R}_{15}$ do not contain $-\text{SO}_3\text{M}$ group, A contains $-\text{SO}_3\text{M}$ group; $\text{R}_{12} - \text{R}_{15}$ represent hydrogen atom, hydroxyl group, aryloxy group, heterocyclic ring, alkylthio group, heterocyclicthio group, arylthio

group, amino group, alkylamino group, arylamino group, heterocyclicamino group, aralkylamino group, mercapto group or halogen atom, alkyl group or alkoxy group; and W represents -CH= or -N=.

3. A light sensitive material according to claim 1 wherein the amount of the sensitizing dye is 1×10^{-5} - 1×10^{-2} mole for 1 mole of silver halide.

4. A light sensitive material according to claim 1 wherein the silver halide comprises at least 50 mole % of silver chloride.

5. A light sensitive material according to claim 1 wherein the silver halide emulsion contains compounds of metals of Group VIII of the periodic table.

6. A light sensitive material according to claim 2 wherein the amount of the compound is 1×10^{-4} - 1×10^{-1} mole for 1 mole of silver halide.

7. A light sensitive material according to claim 1 wherein a subbing layer and/or an undercoat layer are provided between the silver halide emulsion layer and the support.

8. A lithographic printing plate made from the light sensitive material of claim 1.

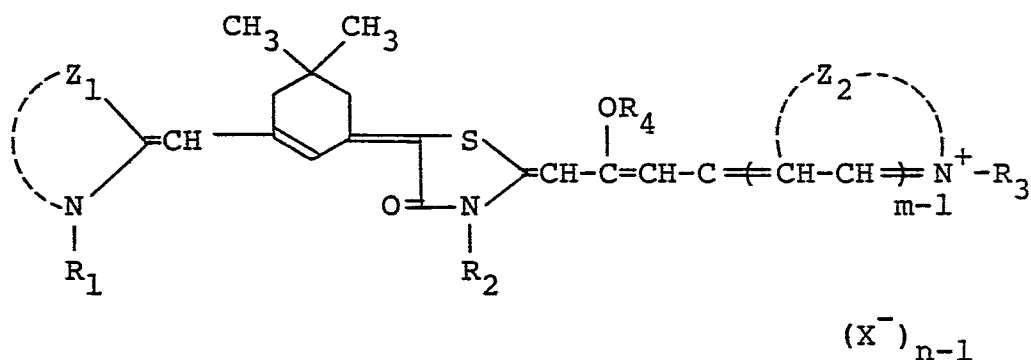
9. A plate making method which comprises imagewise exposing the light sensitive material of claim 1 and then developing it with a diffusion transfer developer.

10. A plate making method according to claim 9 wherein the imagewise exposure is carried out with a

semiconductor laser beam.

11. A method of printing which comprises mounting the lithographic printing plate of claim 8 on an offset printing machine and carrying out printing with a damping solution.

12. A light sensitive material which has an emulsion layer which contains a dye represented by the following general formula (VI);



wherein Z₁ represents a group of atoms necessary for forming a thiazole ring, benzothiazole ring or naphthothiazole ring; Z₂ represents a group of atoms necessary for forming a 5- or 6-membered nitrogen containing heterocyclic ring; R₁, R₃ and R₄ represent alkyl group, aralkyl group or alkenyl group; R₂ represents an alkyl group, an aralkyl group, an alkenyl group or an aryl group; X represents an acid anion; and m and n represent 1 or 2.